

## Preparation of linear pentenenitrile

## Description

- 5 The present invention relates to a process for preparing 3-pentenenitrile by isomerizing streams comprising 2-methyl-3-butenitrile.

10 In the preparation of adiponitrile, an important intermediate in nylon production, 1,3-butadiene is initially reacted with hydrogen cyanide in the presence of nickel(0) which is stabilized with phosphorus ligands to give pentenenitriles. In addition to the main products of the hydrocyanation, 3-pentenenitrile and 2-methyl-3-butenitrile, numerous secondary components are also obtained. Examples thereof are 2-pentenenitriles, 2-methyl-2-butenitriles, C<sub>5</sub>-nitriles and methylglutaronitrile. 2-methyl-3-butenitrile is formed in significant amounts. Depending on the catalyst used, the  
15 molar ratio of 2-methyl-3-butenitrile formed to 3-pentenenitrile may be up to 2:1.

In a second hydrocyanation, 3-pentenenitrile is subsequently reacted with hydrogen cyanide to give adiponitrile over the same nickel catalyst with addition of a Lewis acid. For the second hydrocyanation, it is essential that the 3-pentenenitrile is substantially  
20 free of 2-methyl-3-butenitrile. A hydrocyanation of 2-methyl-3-butenitrile would lead to methylglutaronitrile which constitutes an undesired by-product. Accordingly, in an economic process for preparing adiponitrile, there has to be a separation of 3-pentenenitrile and 2-methyl-3-butenitrile.

25 In order to likewise be able to utilize 2-methyl-3-butenitrile for the preparation of adiponitrile, processes have been proposed for isomerizing 2-methyl-3-butenitrile to linear pentenenitrile, especially 3-pentenenitrile.

For instance, US 3,676,481 describes the discontinuous, batchwise isomerization of 2-methyl-3-butenitrile in the presence of Ni(0), a phosphite ligand and certain Lewis  
30 acids. After the isomerization, the resulting product mixture is distilled off from the catalyst system. A disadvantage in this process is that of the high residence times during the isomerization, the high thermal stress on the thermally sensitive catalyst during the isomerization and during the subsequent distillation. The high thermal stress  
35 on the catalyst leads to undesired degradation of the catalyst.

The German patent application DE 103 11 119.0 to BASF AG, which has an earlier priority date but was unpublished at the priority date of the present application, describes a process for isomerizing 2-methyl-3-butenitrile to linear pentenenitrile in  
40 the presence of a system comprising Ni(0) catalysts and Lewis acids. In this case, a mixture comprising 2-methyl-3-butenitrile and linear pentenenitrile is withdrawn distillatively from the reaction mixture during the isomerization. A disadvantage in this

process is that the product stream withdrawn still contains distinct amounts of unconverted 2-methyl-3-butenenitrile.

It is common to all known processes for isomerizing 2-methyl-3-butenenitrile that 2-methyl-3-butenenitrile cannot be fully converted to 3-pentenitrile owing to the position of the thermodynamic equilibrium. Unconverted 2-methyl-3-butenenitrile has to be fed to the isomerization step for economic performance of the process. However, in the isomerization of 2-methyl-3-butenenitrile, (Z)-2-methyl-2-butenenitrile is obtained as a by-product and would accumulate in the cycle stream in the case of recycling of 2-methyl-3-butenenitrile, since, in the course of the removal of 3-pentenitrile from the isomerization product stream by distillation, it would distill over together with the 2-methyl-3-butenenitrile owing to the very similar vapor pressures.

US 3,865,865 describes the removal of 2-methyl-2-butenenitrile from a mixture with 2-methyl-3-butenenitrile. The removal is carried out by treating the mixture of the nitriles with an aqueous solution which consists of sulfite and bisulfite ions. This forms the bisulfite adduct of 2-methyl-2-butenenitrile which transfers to the aqueous phase. The resulting organic phase is depleted to 50% of the original content of 2-methyl-2-butenenitrile. The process of US 3,865,865 is laborious, since a phase separation of an organic from an aqueous phase is required. Furthermore, this separation can only be integrated with difficulty into an overall process for preparing adiponitrile. An additional disadvantage in this process is that the resulting organic phase first has to be fully freed of water before further use in hydrocyanation reactions using nickel(0) catalysts with phosphorus(III) ligands, since the phosphorus(III) ligands are otherwise irreversibly hydrolyzed and thus inactivated. Another disadvantage in this process is that the resulting bisulfite adducts, for the purpose of reuse of the conjugated nitriles, as described in US 3,865,865, can only be dissociated under drastic conditions and only with moderate yield.

It is thus an object of the present invention to provide a process for preparing 3-pentenitrile by isomerizing 2-methyl-3-butenenitrile, wherein the catalyst for isomerization can be removed from the reaction mixture in a simple manner and recycled, and both the removal of (Z)-2-methyl-2-butenenitrile from 2-methyl-3-butenenitrile and the recycling of the 2-methyl-3-butenenitrile depleted in (Z)-2-methyl-2-butenenitrile are enabled. The process should preferably be simple and economic to carry out and be incorporable into an overall process for preparing adiponitrile.

This object is achieved in accordance with the invention by a process for preparing 3-pentenitrile.

**Embodiment I**

In one embodiment I, the process is characterized by the following process steps:

- 5 (a) isomerizing a reactant stream which comprises 2-methyl-3-butenenitrile over at least one dissolved or dispersed isomerization catalyst to give a stream 1 which comprises the at least one isomerization catalyst, 2-methyl-3-butenenitrile, 3-pentenitrile and (Z)-2-methyl-2-butenenitrile,
- 10 (b) distilling stream 1 to obtain a stream 2 as the top product which comprises 2-methyl-3-butenenitrile, 3-pentenitrile and (Z)-2-methyl-2-butenenitrile, and a stream 3 as the bottom product which comprises the at least one isomerization catalyst,
- 15 (c) distilling stream 2 to obtain a stream 4 as the top product which, compared to stream 2, is enriched in (Z)-2-methyl-2-butenenitrile, based on the sum of all pentenenitriles in stream 2, and a stream 5 as the bottom product which, compared to stream 2, is enriched in 3-pentenitrile and 2-methyl-3-butenenitrile, based on the sum of all pentenenitriles in stream 2,
- 20 (d) distilling stream 5 to obtain a stream 6 as the bottom product which comprises 3-pentenitrile and a stream 7 as the top product which comprises 2-methyl-3-butenenitrile.

25 *Reactant stream*

In process step (a), an isomerization of a reactant stream which comprises 2-methyl-3-butenenitrile takes place over at least one isomerization catalyst.

- 30 In a particular embodiment of the process according to the invention, the reactant stream is obtainable by the following process steps:
- (e) hydrocyanating 1,3-butadiene over at least one hydrocyanation catalyst using hydrogen cyanide to obtain a stream 8 which comprises the at least one hydrocyanation catalyst, 3-pentenitrile, 2-methyl-3-butenenitrile, 1,3-butadiene and residues of hydrogen cyanide,
- 35 (f) distilling stream 8 once or more than once to obtain a stream 9 which comprises 1,3-butadiene, a stream 10 which comprises the at least one hydrocyanation catalyst, and a stream 11 which comprises 3-pentenitrile and 2-methyl-3-butenenitrile,
- 40

- (g) distilling stream 11 to obtain a stream 12 as the bottom product which comprises 3-pentenenitrile, and a stream 13 as the top product which comprises 2-methyl-3-butenenitrile.

5 In process step (e), the reactant stream is prepared by a hydrocyanation of 1,3-butadiene initially taking place over at least one hydrocyanation catalyst using hydrogen cyanide to obtain a stream 8 which comprises the at least one hydrocyanation catalyst, 3-pentenenitrile, 2-methyl-3-butenenitrile and unconverted 1,3-butadiene.

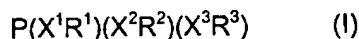
10

The hydrocyanation catalyst used is preferably a homogeneous nickel(0) catalyst which is stabilized with phosphorus ligands.

15 The phosphorus ligands of the nickel(0) complexes and the free phosphorus ligands are preferably selected from mono- or bidentate phosphines, phosphites, phosphinites and phosphonites.

These phosphorus ligands preferably have the formula I

20



In the context of the present invention, compound I is a single compound or a mixture of different compounds of the aforementioned formula.

25 According to the invention,  $X^1$ ,  $X^2$ ,  $X^3$  each independently are oxygen or a single bond. When all of the  $X^1$ ,  $X^2$  and  $X^3$  groups are single bonds, compound I is a phosphine of the formula  $P(R^1 R^2 R^3)$  with the definitions of  $R^1$ ,  $R^2$  and  $R^3$  specified in this description.

30 When two of the  $X^1$ ,  $X^2$  and  $X^3$  groups are single bonds and one is oxygen, compound I is a phosphinite of the formula  $P(OR^1)(R^2)(R^3)$  or  $P(R^1)(OR^2)(R^3)$  or  $P(R^1)(R^2)(OR^3)$  with the definitions of  $R^1$ ,  $R^2$  and  $R^3$  specified below.

35 When one of the  $X^1$ ,  $X^2$  and  $X^3$  groups is a single bond and two are oxygen, compound I is a phosphonite of the formula  $P(OR^1)(OR^2)(R^3)$  or  $P(R^1)(OR^2)(OR^3)$  or  $P(OR^1)(R^2)(OR^3)$  with the definitions of  $R^1$ ,  $R^2$  and  $R^3$  specified in this description.

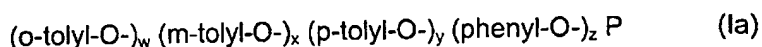
40 In a preferred embodiment, all  $X^1$ ,  $X^2$  and  $X^3$  groups should be oxygen, so that compound I is advantageously a phosphite of the formula  $P(OR^1)(OR^2)(OR^3)$  with the definitions of  $R^1$ ,  $R^2$  and  $R^3$  specified below.

According to the invention,  $R^1$ ,  $R^2$ ,  $R^3$  are each independently identical or different organic radicals.  $R^1$ ,  $R^2$  and  $R^3$  are each independently alkyl radicals preferably having from 1 to 10 carbon atoms, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, aryl groups such as phenyl, o-tolyl, m-tolyl, p-tolyl, 1-naphthyl, 2-naphthyl, or hydrocarbyl, preferably having from 1 to 20 carbon atoms, such as 1,1'-biphenol, 1,1'-binaphthol. The  $R^1$ ,  $R^2$  and  $R^3$  groups may be bonded together directly, i.e. not solely via the central phosphorus atom. Preference is given to the  $R^1$ ,  $R^2$  and  $R^3$  groups not being bonded together directly.

10 In a preferred embodiment,  $R^1$ ,  $R^2$  and  $R^3$  groups are radicals selected from the group consisting of phenyl, o-tolyl, m-tolyl and p-tolyl. In a particularly preferred embodiment, a maximum of two of the  $R^1$ ,  $R^2$  and  $R^3$  groups should be phenyl groups.

In another preferred embodiment, a maximum of two of the  $R^1$ ,  $R^2$  and  $R^3$  groups should be o-tolyl groups.

Particularly preferred compounds I which may be used are those of the formula Ia



20 where w, x, y, z are each a natural number, and the following conditions apply:  
 $w + x + y + z = 3$  and  $z \leq 2$ .

Such compounds Ia are, for example, (p-tolyl-O)(phenyl-O)<sub>2</sub>P, (m-tolyl-O)(phenyl-O)<sub>2</sub>P, (o-tolyl-O)(phenyl-O)<sub>2</sub>P, (p-tolyl-O)<sub>2</sub>(phenyl-O)P, (m-tolyl-O)<sub>2</sub>(phenyl-O)P, (o-tolyl-O)<sub>2</sub>(phenyl-O)P, (m-tolyl-O)(p-tolyl-O)(phenyl-O)P, (o-tolyl-O)(p-tolyl-O)(phenyl-O)P, (o-tolyl-O)(m-tolyl-O)(phenyl-O)P, (p-tolyl-O)<sub>3</sub>P, (m-tolyl-O)(p-tolyl-O)<sub>2</sub>P, (o-tolyl-O)(p-tolyl-O)<sub>2</sub>P, (m-tolyl-O)<sub>2</sub>(p-tolyl-O)P, (o-tolyl-O)<sub>2</sub>(p-tolyl-O)P, (o-tolyl-O)(m-tolyl-O)(p-tolyl-O)P, (m-tolyl-O)<sub>3</sub>P, (o-tolyl-O)(m-tolyl-O)<sub>2</sub>P (o-tolyl-O)<sub>2</sub>(m-tolyl-O)P or mixtures of such compounds.

30 Mixtures comprising (m-tolyl-O)<sub>3</sub>P, (m-tolyl-O)<sub>2</sub>(p-tolyl-O)P, (m-tolyl-O)(p-tolyl-O)<sub>2</sub>P and (p-tolyl-O)<sub>3</sub>P may be obtained, for example, by reacting a mixture comprising m-cresol and p-cresol, in particular in a molar ratio of 2:1, as obtained in the distillative workup of crude oil, with a phosphorus trihalide, such as phosphorus trichloride.

35 In another, likewise preferred embodiment, the phosphorus ligands are the phosphites, described in detail in DE-A 199 53 058, of the formula I b:



40 where

- 5  $R^1$ : aromatic radical having a  $C_1$ - $C_{18}$ -alkyl substituent in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system, or having an aromatic substituent in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system, or having a fused aromatic system in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system,
- 10  $R^2$ : aromatic radical having a  $C_1$ - $C_{18}$ -alkyl substituent in the m-position to the oxygen atom which joins the phosphorus atom to the aromatic system, or having an aromatic substituent in the m-position to the oxygen atom which joins the phosphorus atom to the aromatic system, or having a fused aromatic system in the m-position to the oxygen atom which joins the phosphorus atom to the aromatic system, the aromatic radical bearing a hydrogen atom in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system,
- 15  $R^3$ : aromatic radical having a  $C_1$ - $C_{18}$ -alkyl substituent in the p-position to the oxygen atom which joins the phosphorus atom to the aromatic system, or having an aromatic substituent in the p-position to the oxygen atom which joins the phosphorus atom to the aromatic system, the aromatic radical bearing a hydrogen atom in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system,
- 20  $R^4$ : aromatic radical which bears substituents other than those defined for  $R^1$ ,  $R^2$  and  $R^3$  in the o-, m- and p-position to the oxygen atom which joins the phosphorus atom to the aromatic system, the aromatic radical bearing a hydrogen atom in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system,
- 25  $x$ : 1 or 2,
- 30  $y, z, p$ : each independently 0, 1 or 2, with the proviso that  $x+y+z+p=3$ .

35 Preferred phosphites of the formula I b can be taken from DE-A 199 53 058. The  $R^1$  radical may advantageously be o-tolyl, o-ethylphenyl, o-n-propylphenyl, o-isopropylphenyl, o-n-butylphenyl, o-sec-butylphenyl, o-tert-butylphenyl, (o-phenyl)phenyl or 1-naphthyl groups.

40 Preferred  $R^2$  radicals are m-tolyl, m-ethylphenyl, m-n-propylphenyl, m-isopropylphenyl, m-n-butylphenyl, m-sec-butylphenyl, m-tert-butylphenyl, (m-phenyl)phenyl or 2-naphthyl groups.

Advantageous  $R^3$  radicals are p-tolyl, p-ethylphenyl, p-n-propylphenyl, p-isopropylphenyl, p-n-butylphenyl, p-sec-butylphenyl, p-tert-butylphenyl or (p-phenyl)phenyl groups.

- 5 The  $R^4$  radical is preferably phenyl. p is preferably zero. For the indices x, y, z and p in compound I b, there are the following possibilities:

x	y	z	p
1	0	0	2
1	0	1	1
1	1	0	1
2	0	0	1
1	0	2	0
1	1	1	0
1	2	0	0
2	0	1	0
2	1	0	0

- 10 Preferred phosphites of the formula I b are those in which p is zero, and  $R^1$ ,  $R^2$  and  $R^3$  are each independently selected from o-isopropylphenyl, m-tolyl and p-tolyl, and  $R^4$  is phenyl.

- 15 Particularly preferred phosphites of the formula I b are those in which  $R^1$  is the o-isopropylphenyl radical,  $R^2$  is the m-tolyl radical and  $R^3$  is the p-tolyl radical with the indices specified in the table above; also those in which  $R^1$  is the o-tolyl radical,  $R^2$  is the m-tolyl radical and  $R^3$  is the p-tolyl radical with the indices specified in the table; additionally those in which  $R^1$  is the 1-naphthyl radical,  $R^2$  is the m-tolyl radical and  $R^3$  is the p-tolyl radical with the indices specified in the table; also those in which  $R^1$  is the o-tolyl radical,  $R^2$  is the 2-naphthyl radical and  $R^3$  is the p-tolyl radical with the indices specified in the table; and finally those in which  $R^1$  is the o-isopropylphenyl radical,  $R^2$  is the 2-naphthyl radical and  $R^3$  is the p-tolyl radical with the indices specified in the table; and also mixtures of these phosphites.

Phosphites of the formula I b may be obtained by

- 25 a) reacting a phosphorus trihalide with an alcohol selected from the group consisting of  $R^1OH$ ,  $R^2OH$ ,  $R^3OH$  and  $R^4OH$  or mixtures thereof to obtain a dihalophosphorous monoester,
- 30 b) reacting the dihalophosphorous monoester mentioned with an alcohol selected from the group consisting of  $R^1OH$ ,  $R^2OH$ ,  $R^3OH$  and  $R^4OH$  or mixtures thereof to obtain a monohalophosphorous diester and

- c) reacting the monohalophosphorous diester mentioned with an alcohol selected from the group consisting of  $R^1OH$ ,  $R^2OH$ ,  $R^3OH$  and  $R^4OH$  or mixtures thereof to obtain a phosphite of the formula I b.

5

The reaction may be carried out in three separate steps. Equally, two of the three steps may be combined, i.e. a) with b) or b) with c). Alternatively, all of steps a), b) and c) may be combined together.

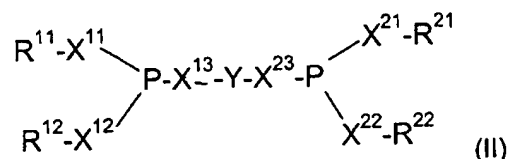
- 10 Suitable parameters and amounts of the alcohols selected from the group consisting of  $R^1OH$ ,  $R^2OH$ ,  $R^3OH$  and  $R^4OH$  or mixtures thereof may be determined readily by a few simple preliminary experiments.

- 15 Useful phosphorus trihalides are in principle all phosphorus trihalides, preferably those in which the halide used is Cl, Br, I, in particular Cl, and mixtures thereof. It is also possible to use mixtures of various identically or differently halogen-substituted phosphines as the phosphorus trihalide. Particular preference is given to  $PCl_3$ . Further details on the reaction conditions in the preparation of the phosphites I b and for the workup can be taken from DE-A 199 53 058.

20

The phosphites I b may also be used in the form of a mixture of different phosphites I b as a ligand. Such a mixture may be obtained, for example, in the preparation of the phosphites I b.

- 25 However, preference is given to the phosphorus ligand being multidentate, in particular bidentate. The ligand used therefore preferably has the formula II



where

30

$X^{11}, X^{12}, X^{13}, X^{21}, X^{22}, X^{23}$  are each independently oxygen or a single bond  
 $R^{11}, R^{12}$  are each independently identical or different,

separate or bridged organic radicals

$R^{21}, R^{22}$

are each independently identical or different, separate or  
 bridged organic radicals,

35

Y

is a bridging group.

In the context of the present invention, compound II is a single compound or a mixture of different compounds of the aforementioned formula.

5 In a preferred embodiment,  $X^{11}$ ,  $X^{12}$ ,  $X^{13}$ ,  $X^{21}$ ,  $X^{22}$ ,  $X^{23}$  may each be oxygen. In such a case, the bridging group Y is bonded to phosphite groups.

10 In another preferred embodiment,  $X^{11}$  and  $X^{12}$  may each be oxygen and  $X^{13}$  a single bond, or  $X^{11}$  and  $X^{13}$  each oxygen and  $X^{12}$  a single bond, so that the phosphorus atom surrounded by  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  is the central atom of a phosphonite. In such a case,  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be oxygen, or  $X^{21}$  and  $X^{22}$  may each be oxygen and  $X^{23}$  a single bond, or  $X^{21}$  and  $X^{23}$  may each be oxygen and  $X^{22}$  a single bond, or  $X^{23}$  may be oxygen and  $X^{21}$  and  $X^{22}$  each a single bond, or  $X^{21}$  may be oxygen and  $X^{22}$  and  $X^{23}$  each a single bond, or  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may be the central atom of a phosphite, phosphonite, phosphinite or phosphine, preferably a phosphonite.

20 In another preferred embodiment,  $X^{13}$  may be oxygen and  $X^{11}$  and  $X^{12}$  each a single bond, or  $X^{11}$  may be oxygen and  $X^{12}$  and  $X^{13}$  each a single bond, so that the phosphorus atom surrounded by  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  is the central atom of a phosphonite. In such a case,  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be oxygen, or  $X^{23}$  may be oxygen and  $X^{21}$  and  $X^{22}$  each a single bond, or  $X^{21}$  may be oxygen and  $X^{22}$  and  $X^{23}$  each a single bond, or  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may be the central atom of a phosphite, phosphinite or phosphine, preferably a phosphinite.

25 In another preferred embodiment,  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  is the central atom of a phosphine. In such a case,  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be oxygen, or  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may be the central atom of a phosphite or phosphine, preferably a phosphine.

35 The bridging group Y is preferably an aryl group which is substituted, for example by  $C_1$ - $C_4$ -alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or is unsubstituted, preferably a group having from 6 to 20 carbon atoms in the aromatic system, in particular pyrocatechol, bis(phenol) or bis(naphthol).

40 The  $R^{11}$  and  $R^{12}$  radicals may each independently be identical or different organic radicals. Advantageous  $R^{11}$  and  $R^{12}$  radicals are aryl radicals, preferably those having from 6 to 10 carbon atoms, which may be unsubstituted or mono- or polysubstituted, in

particular by C<sub>1</sub>-C<sub>4</sub>-alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or unsubstituted aryl groups.

- 5 The R<sup>21</sup> and R<sup>22</sup> radicals may each independently be the same or different organic radicals. Advantageous R<sup>21</sup> and R<sup>22</sup> radicals are aryl radicals, preferably those having from 6 to 10 carbon atoms, which may be unsubstituted or mono- or polysubstituted, in particular by C<sub>1</sub>-C<sub>4</sub>-alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or unsubstituted aryl groups.
- 10 The R<sup>11</sup> and R<sup>12</sup> radicals may each be separate or bridged. The R<sup>21</sup> and R<sup>22</sup> radicals may also each be separate or bridged. The R<sup>11</sup>, R<sup>12</sup>, R<sup>21</sup> and R<sup>22</sup> radicals may each be separate, two may be bridged and two separate, or all four may be bridged, in the manner described.
- 15 In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV and V specified in US 5,723,641. In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV, V, VI and VII specified in US 5,512,696, in particular the compounds used there in examples 1 to 31. In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV and XV specified in US 5,821,378, in particular the compounds used there in examples 1 to 73.
- 20 In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV, V and VI specified in US 5,512,695, in particular the compounds used there in examples 1 to 6. In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII and XIV specified in US 5,981,772, in particular the compounds used there in examples 1 to 66.
- 30 In a particularly preferred embodiment, useful compounds are those specified in US 6,127,567 and the compounds used there in examples 1 to 29. In a particularly preferred embodiment, useful compounds are those of the formula I, II, III, IV, V, VI, VII, VIII, IX and X specified in US 6,020,516, in particular the compounds used there in examples 1 to 33. In a particularly preferred embodiment, useful compounds are those specified in US 5,959,135, and the compounds used there in examples 1 to 13.
- 35 In a particularly preferred embodiment, useful compounds are those of the formula I, II and III specified in US 5,847,191. In a particularly preferred embodiment, useful compounds are those specified in US 5,523,453, in particular the compounds illustrated there in formula 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 and 21. In a particularly preferred embodiment, useful compounds are those
- 40

specified in WO 01/14392, preferably the compounds illustrated there in formula V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV, XV, XVI, XVII, XXI, XXII, XXIII.

5 In a particularly preferred embodiment, useful compounds are those specified in WO 98/27054. In a particularly preferred embodiment, useful compounds are those specified in WO 99/13983. In a particularly preferred embodiment, useful compounds are those specified in WO 99/64155.

10 In a particularly preferred embodiment, useful compounds are those specified in the German patent application DE 100 380 37. In a particularly preferred embodiment, useful compounds are those specified in the German patent application DE 100 460 25. In a particularly preferred embodiment, useful compounds are those specified in the German patent application DE 101 502 85.

15 In a particularly preferred embodiment, useful compounds are those specified in the German patent application DE 101 502 86. In a particularly preferred embodiment, useful compounds are those specified in the German patent application DE 102 071 65. In a further particularly preferred embodiment of the present invention, useful phosphorus chelate ligands are those specified in US 2003/0100442 A1.

20 In a further particularly preferred embodiment of the present invention, useful phosphorus chelate ligands are those specified in the German patent application reference number DE 103 50 999.2 of 10.30.2003 which has an earlier priority date but had not been published at the priority date of the present application.

25 The compounds I, Ia, Ib and II described and their preparation are known per se. Phosphorus ligands used may also be a mixture comprising at least two of the compounds I, Ia, Ib and II.

30 In a particularly preferred embodiment of the process according to the invention, the phosphorus ligand of the nickel(0) complex and/or the free phosphorus ligand is selected from tritolyl phosphite, bidentate phosphorus chelate ligands and the phosphites of the formula I b

35 
$$P(O-R^1)_x(O-R^2)_y(O-R^3)_z(O-R^4)_p \quad (I\ b)$$

where  $R^1$ ,  $R^2$  and  $R^3$  are each independently selected from o-isopropylphenyl, m-tolyl and p-tolyl,  $R^4$  is phenyl; x is 1 or 2, and y, z, p are each independently 0, 1 or 2 with the proviso that  $x+y+z+p = 3$ ; and mixtures thereof.

40 Process step (e) may be carried out in any suitable apparatus known to those skilled in the art. Useful apparatus for the reaction is thus customary apparatus, as described, for

example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 20, John Wiley & Sons, New York, 1996, pages 1040 to 1055, such as stirred tank reactors, loop reactors, gas circulation reactors, bubble columns or tubular reactors, in each case, if appropriate, with apparatus to remove heat of reaction. The reaction may be carried out in a plurality of, such as two or three, apparatuses.

In a preferred embodiment of the process according to the invention, advantageous reactors have been found to be reactors having backmixing characteristics or batteries of reactors having backmixing characteristics. It has been found that batteries of reactors having backmixing characteristics which are operated in crossflow mode with regard to the metering of hydrogen cyanide are particularly advantageous.

The hydrocyanation may be carried out in the presence or in the absence of a solvent. When a solvent is used, the solvent should be liquid at the given reaction temperature and the given reaction pressure and inert toward the unsaturated compounds and the at least one catalyst. In general, the solvents used are hydrocarbons, for example benzene or xylene, or nitriles, for example acetonitrile or benzonitrile. However, preference is given to using a ligand as the solvent.

The reaction may be carried out in batch mode, continuously or in semibatch operation.

The hydrocyanation reaction may be carried out by charging the apparatus with all reactants. However, it is preferred when the apparatus is filled with the catalyst, the unsaturated organic compound and, if appropriate, the solvent. The gaseous hydrogen cyanide preferably floats over the surface of the reaction mixture or is passed through the reaction mixture. A further procedure for charging the apparatus is the filling of the apparatus with the catalyst, hydrogen cyanide and, if appropriate, the solvent, and slowly metering the unsaturated compound into the reaction mixture. Alternatively, it is also possible that the reactants are introduced into the reactor and the reaction mixture is brought to the reaction temperature at which the hydrogen cyanide is added to the mixture in liquid form. In addition, the hydrogen cyanide may also be added before heating to reaction temperature. The reaction is carried out under conventional hydrocyanation conditions for temperature, atmosphere, reaction time, etc.

Preference is given to carrying out the hydrocyanation continuously in one or more stirred process steps. When a multitude of process steps is used, preference is given to the process steps being connected in series. In this case, the product is transferred from one process step directly into the next process step. The hydrogen cyanide may be fed directly into the first process step or between the individual process steps.

When the process according to the invention is carried out in semibatch operation, preference is given to initially charging the catalyst components and 1,3-butadiene in

the reactor, while hydrogen cyanide is metered into the reaction mixture over the reaction time.

5 The reaction is preferably carried out at absolute pressures of from 0.1 to 500 MPa, more preferably from 0.5 to 50 MPa, in particular from 1 to 5 MPa. The reaction is preferably carried out at temperatures of from 273 to 473 K, more preferably from 313 to 423 K, in particular from 333 to 393 K. Advantageous average mean residence times of the liquid reactor phase have been found to be in the range from 0.001 to 100 hours, preferably from 0.05 to 20 hours, more preferably from 0.1 to 5 hours, in each case per  
10 reactor.

In one embodiment, the reaction may be performed in the liquid phase in the presence of a gas phase and, if appropriate, of a solid suspended phase. The starting materials, hydrogen cyanide and 1,3-butadiene, may each be metered in in liquid or gaseous  
15 form.

In a further embodiment, the reaction may be carried out in liquid phase, in which case the pressure in the reactor is such that all feedstocks such as 1,3-butadiene, hydrogen cyanide and the at least one catalyst are metered in in liquid form and are in the liquid  
20 phase in the reaction mixture. A solid suspended phase may be present in the reaction mixture and may also be metered in together with the at least one catalyst, for example consisting of degradation products of the catalyst system comprising nickel(II) compounds inter alia.

25 In process step (e), a stream 8 which comprises 3-pentenitrile, 2-methyl-3-butenitrile, the at least one catalyst and unconverted 1,3-butadiene is obtained.

Stream 8 which comprises 3-pentenitrile, 2-methyl-3-butenitrile, the at least one catalyst and unconverted 1,3-butadiene is subsequently transferred in process step (f) to a distillation apparatus. In this distillation apparatus, stream 8 is distilled once or  
30 more than once to obtain a stream 9 which comprises 1,3-butadiene, a stream 10 which comprises the at least one hydrocyanation catalyst, and a stream 11 which comprises 3-pentenitrile and 2-methyl-3-butenitrile.

35 The distillation of process step (f) may be effected in two stages, as described in DE-A-102 004 004 720, process steps (b) and (c). The distillation of process step (f) may also be effected according to DE-A-102 004 004 729, process steps (b) and (c).

The distillation(s) of process step (f) may be carried out in any suitable apparatus  
40 known to those skilled in the art. Suitable apparatus for distillation is described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-

cap tray columns, columns having structured packing or random packing, which may also be operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporating, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensation of the vapor stream. The individual distillations can each be carried out in a plurality of, such as two or three, apparatuses, advantageously in a single apparatus in each case.

The distillation(s) may additionally each be effected in one stage in the case of a partial evaporation of the feed stream.

The pressure in process step (f) is preferably from 0.001 to 10 bar, more preferably from 0.010 to 1 bar, in particular from 0.02 to 0.5 bar. The distillation(s) is/are carried out in such a way that the temperature(s) in the bottom of the distillation apparatus(es) is/are preferably from 30 to 200°C, more preferably from 50 to 150°C, in particular from 60 to 120°C. The distillation(s) is/are carried out in such a way that the condensation temperatures at the top of the distillation apparatus are preferably from -50 to 150°C, more preferably from -15 to 60°C, in particular from 5 to 45°C. In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained both at the top and in the bottom of the distillation apparatus(es).

Stream 11 is subsequently subjected to a distillation in a further process step (g). This distillation may be carried out in any suitable apparatus known to those skilled in the art. Suitable apparatus for distillation is described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or random packing, which may also be operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporating, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensation of the vapor stream. The distillation can be carried out in a plurality of, such as two or three, apparatuses, advantageously in a single apparatus. The distillation may additionally be effected in one stage in the case of a partial evaporation of the feed stream.

The pressure in process step (g) is preferably from 0.001 to 100 bar, more preferably from 0.01 to 20 bar, in particular from 0.05 to 2 bar. The distillation is carried out in such a way that the temperature in the bottom of the distillation apparatus is preferably from 30 to 250°C, more preferably from 50 to 200°C, in particular from 60 to 180°C. The distillation is carried out in such a way that the condensation temperature at the top of the distillation apparatus is preferably from -50 to 250°C, more preferably from

0 to 180°C, in particular from 15 to 160°C. In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained both at the top and in the bottom of the distillation apparatus.

- 5 In process step (g), a stream 12 is obtained as the bottom product which comprises 1,3-pentenenitrile, and stream 13 as the top product which comprises 2-methyl-3-butenenitrile. Stream 13 is preferably used as the reactant stream in the process according to the invention for preparing 3-pentenenitrile.
- 10 In further preferred embodiments of the process according to the invention, stream 8 obtained in process step (e) is transferred directly to process step (g). In this process step (g), a stream is then obtained via the bottom and comprises substantially 3-pentenenitrile and the at least one hydrocyanation catalyst. In addition, a stream is obtained overhead which comprises substantially 2-methyl-3-butenenitrile and 1,3-
- 15 butadiene. This 2-methyl-3-butenenitrile- and 1,3-butadiene-rich stream may likewise be used as the reactant stream in the process according to the invention for preparing 3-pentenenitrile. If this reactant stream is used in the process according to the invention, the content of 2-methyl-3-butenenitrile in this stream is preferably from 10 to 90% by weight, more preferably from 20 to 85% by weight, in particular from 30 to 80%
- 20 by weight, based in each case on the stream.

- Alternatively, it is also possible to deplete stream 8 obtained in process step (e) only in 1,3-butadiene in process step (f). Via the bottom of process step (f) is then obtained a stream 11a which comprises substantially 3-pentenenitrile, 2-methyl-3-butenenitrile and
- 25 the at least one hydrocyanation catalyst. In that case, this stream 11a is subsequently worked up further in process step (g) with removal of 3-pentenenitrile and the at least one hydrocyanation catalyst on the one hand, and also of 2-methyl-3-butenenitrile on the other. Stream 13a stemming from process step (g) at the top of the distillation comprises substantially 2-methyl-3-butenenitrile. This stream 13a may likewise be used
- 30 as the reactant stream in the process according to the invention for preparing 3-pentenenitrile.

- In a further embodiment, stream 8 from process step (e) is depleted only in 1,3-butadiene in process step (f) and transferred to process step (g), where a stream 12
- 35 comprising 3-pentenenitrile and the hydrocyanation catalyst is obtained in the bottom.

- In a further embodiment of the present invention, a reactant stream is used which stems from a hydrocyanation of process step (e) and a subsequent workup in process step (f), in which case, if appropriate, only a depletion in 1,3-butadiene is undertaken in
- 40 process step (f). The stream 11b resulting therefrom is subsequently transferred into process step (a) of the process according to the invention. The hydrocyanation catalyst present in this stream 11b is then preferably used as the at least one isomerization

catalyst in process step (a) of the process according to the invention. It is possible to additionally add a suitable Lewis acid, as described, for example, in DE-A-102 004 004 696.

- 5 In a further embodiment of the present invention, it is possible that the reactant stream used in the inventive process step (a) corresponds to stream 11 of process step (f), so that a separation of stream 11 in process step (g) is dispensed with.

10 In a further embodiment of the process according to the invention, the reactant stream used is stream 8 which stems from process step (e). In this case, process steps (f) and (g) are thus dispensed with in the preparation of the reactant stream for the process according to the invention.

*Process step (a)*

15 In process step (a), an isomerization of the reactant stream which comprises 2-methyl-3-butenitrile takes place over at least one isomerization catalyst. This gives a stream 1 which comprises the isomerization catalyst, unconverted 2-methyl-3-butenitrile, 3-pentenitrile and (Z)-2-methyl-2-butenitrile.

20 According to the invention, the isomerization is carried out in the presence of a system comprising

- 25 a) nickel(0),  
b) a compound which contains trivalent phosphorus and complexes nickel(0) as a ligand and, if appropriate,  
c) a Lewis acid.

30 Nickel(0)-containing catalyst systems can be prepared by processes known per se.

35 The ligands for the isomerization catalyst may be the same phosphorus ligands as used for the hydrocyanation catalyst used in process step (e). The hydrocyanation catalyst may thus be identical to the isomerization catalyst. However, the selection of the ligands for the reactions in process steps (a) and (e) does not necessarily have to be the same.

In addition, the system, if appropriate, comprises a Lewis acid.

40 In the context of the present invention, a Lewis acid refers to a single Lewis acid or a mixture of a plurality of, such as two, three or four, Lewis acids.

Useful Lewis acids are inorganic or organic metal compounds in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include  $\text{ZnBr}_2$ ,  $\text{ZnI}_2$ ,  $\text{ZnCl}_2$ ,  $\text{ZnSO}_4$ ,  $\text{CuCl}_2$ ,  $\text{CuCl}$ ,  $\text{Cu}(\text{O}_3\text{SCF}_3)_2$ ,  $\text{CoCl}_2$ ,  $\text{CoI}_2$ ,  $\text{FeI}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{FeCl}_2(\text{THF})_2$ ,  $\text{TiCl}_4(\text{THF})_2$ ,  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{ClTi}(\text{O-i-propyl})_3$ ,  $\text{MnCl}_2$ ,  $\text{ScCl}_3$ ,  $\text{AlCl}_3$ ,  $(\text{C}_8\text{H}_{17})\text{AlCl}_2$ ,  $(\text{C}_8\text{H}_{17})_2\text{AlCl}$ ,  $(\text{i-C}_4\text{H}_9)_2\text{AlCl}$ ,  $(\text{C}_6\text{H}_5)_2\text{AlCl}$ ,  $(\text{C}_6\text{H}_5)\text{AlCl}_2$ ,  $\text{ReCl}_5$ ,  $\text{ZrCl}_4$ ,  $\text{NbCl}_5$ ,  $\text{VCl}_3$ ,  $\text{CrCl}_2$ ,  $\text{MoCl}_5$ ,  $\text{YCl}_3$ ,  $\text{CdCl}_2$ ,  $\text{LaCl}_3$ ,  $\text{Er}(\text{O}_3\text{SCF}_3)_3$ ,  $\text{Yb}(\text{O}_2\text{CCF}_3)_3$ ,  $\text{SmCl}_3$ ,  $\text{B}(\text{C}_6\text{H}_5)_3$ ,  $\text{TaCl}_5$ , as described, for example, in US 6,127,567, US 6,171,996 and US 6,380,421. Also useful are metal salts such as  $\text{ZnCl}_2$ ,  $\text{CoI}_2$  and  $\text{SnCl}_2$ , and organometallic compounds such as  $\text{RAlCl}_2$ ,  $\text{R}_2\text{AlCl}$ ,  $\text{RSnO}_3\text{SCF}_3$  and  $\text{R}_3\text{B}$ , where R is an alkyl or aryl group, as described, for example, in US 3,496,217, US 3,496,218 and US 4,774,353. According to US 3,773,809, the promoter used may be a metal in cationic form which is selected from the group consisting of zinc, cadmium, beryllium, aluminum, gallium, indium, thallium, titanium, zirconium, hafnium, erbium, germanium, tin, vanadium, niobium, scandium, chromium, molybdenum, tungsten, manganese, rhenium, palladium, thorium, iron and cobalt, preferably zinc, cadmium, titanium, tin, chromium, iron and cobalt, and the anionic moiety of the compound may be selected from the group consisting of halides such as fluoride, chloride, bromide and iodide, anions of lower fatty acids having from 2 to 7 carbon atoms,  $\text{HPO}_3^{2-}$ ,  $\text{H}_3\text{PO}_2^-$ ,  $\text{CF}_3\text{COO}^-$ ,  $\text{C}_7\text{H}_{15}\text{OSO}_2^-$  or  $\text{SO}_4^{2-}$ . Further suitable promoters, disclosed by US 3,773,809, are borohydrides, organoborohydrides and boric esters of the formula  $\text{R}_3\text{B}$  and  $\text{B}(\text{OR})_3$ , where R is selected from the group consisting of hydrogen, aryl radicals having from 6 to 18 carbon atoms, aryl radicals substituted by alkyl groups having from 1 to 7 carbon atoms and aryl radicals substituted by cyano-substituted alkyl groups having from 1 to 7 carbon atoms, advantageously triphenylboron. Moreover, as described in US 4,874,884, it is possible to use synergistically active combinations of Lewis acids, in order to increase the activity of the catalyst system. Suitable promoters may, for example, be selected from the group consisting of  $\text{CdCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{B}(\text{C}_6\text{H}_5)_3$  and  $(\text{C}_6\text{H}_5)_3\text{SnX}$ , where  $\text{X}=\text{CF}_3\text{SO}_3$ ,  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3$  or  $(\text{C}_6\text{H}_5)_3\text{BCN}$ , and the preferred ratio specified of promoter to nickel is from about 1:16 to about 50:1.

In the context of the present invention, the term Lewis acid also includes the promoters specified in US 3,496,217, US 3,496,218, US 4,774,353, US 4,874,884, US 6,127,567, US 6,171,996 and US 6,380,421.

Particularly preferred Lewis acids among those mentioned are in particular metal salts, more preferably metal halides, such as fluorides, chlorides, bromides, iodides, in particular chlorides, of which particular preference is given to zinc chloride, iron(II) chloride and iron(III) chloride.

The isomerization may be carried out in the presence of a liquid diluent,

- for example a hydrocarbon such as hexane, heptane, octane, cyclohexane, methylcyclohexane, benzene, decahydronaphthalene
- for example an ether such as diethyl ether, tetrahydrofuran, dioxane, glycol dimethyl ether, anisole,
- 5 - for example an ester such as ethyl acetate, methyl benzoate, or
- for example a nitrile such as acetonitrile, benzonitrile, or
- mixtures of such diluents.

10 In a particularly preferred embodiment, a useful isomerization is in the absence of such a liquid diluent.

Moreover, it has been found to be advantageous when the isomerization in process step (a) is carried out in an unoxidizing atmosphere, for example under a protective gas atmosphere composed of nitrogen or a noble gas such as argon.

15 Process step (a) may be carried out in any suitable apparatus known to those skilled in the art. Useful apparatus for this reaction is customary apparatus as described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 20, John Wiley & Sons, New York, 1996, pages 1040 to 1055, such as stirred tank reactors, loop  
20 reactors, gas circulation reactors, bubble column reactors or tubular reactors. The reaction may be carried out in a plurality of, such as two or three, apparatuses.

In a preferred embodiment of the process according to the invention, the isomerization is carried out in a compartmented tubular reactor.

25 In a further preferred embodiment of the process according to the invention, the isomerization is carried out in at least two reactors connected in series, in which case the first reactor has substantially stirred tank characteristics and the second reactor is designed in such a way that it has substantially tubular characteristics.

30 In a particularly preferred embodiment of the process according to the invention, the isomerization is carried out in a reactor, the reactor having the characteristics of a stirred tank battery which corresponds to from 2 to 20 stirred tanks, in particular from 3 to 10 stirred tanks.

35 In one embodiment of the process according to the invention, the reaction may be carried out in one distillation apparatus, in which case the isomerization reaction takes place at least in the bottom region of the distillation apparatus. Any distillation apparatus known to those skilled in the art is suitable, as described, for example, in:  
40 Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or random packing, which may also be

- operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporation, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensing the vapor stream. The distillation with simultaneous reaction can be carried out in a plurality of, such as two or three, apparatuses, advantageously in a single apparatus. The distillation may additionally be effected in one stage in the case of a partial evaporation of the feed stream.
- 10 Process step (a) of the process according to the invention is preferably carried out at an absolute pressure of from 0.1 mbar to 100 bar, more preferably from 1 mbar to 16 bar, in particular from 10 mbar to 6 bar. The temperature in process step (a) is preferably from 25 to 250°C, more preferably from 30 to 180°C, in particular from 40 to 140°C.
- 15 The composition of the stream withdrawn, with regard to the molar ratio of 2-methyl-3-butenitrile to linear pentenenitrile and thus the degree of conversion of 2-methyl-3-butenitrile used, may be adjusted, depending on the composition of the feed stream, in a technically simple manner by the temperature, the catalyst concentration, the residence time and the configuration of the reactor. In a preferred embodiment of the process according to the invention, the degree of conversion is adjusted with the aid of these measures to values in the range from 10 to 99%, more preferably from 30 to 95%, in particular from 60 to 90%.
- 25 *Process step (b)*
- In process step (b), the stream 1 obtained in process step (a) is distilled. This gives a stream 2 which comprises 2-methyl-3-butenitrile, 3-pentenenitrile and (Z)-2-methyl-2-butenitrile as the top product. In addition, a stream 3 is obtained in process step (b) as the bottom product which comprises the at least one isomerization catalyst.
- 30 Process step (b) of the process according to the invention may be carried out in any suitable distillation apparatus known to those skilled in the art. Suitable apparatus for distillation is described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or random packing, which may also be operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporating, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensation of the vapor stream. The distillation can be carried out in a plurality of, such as two or three, apparatuses, advantageously in a single apparatus.
- 40

The distillation may additionally be effected in one stage in the case of a partial evaporation of the feed stream.

5 Process step (b) of the process according to the invention is preferably carried out at an absolute pressure of from 0.1 mbar to 100 bar, more preferably from 1 mbar to 6 bar, in particular from 10 mbar to 500 mbar. The distillation is carried out in such a way that the temperature in the bottom of the distillation apparatus is preferably from 25 to 250°C, more preferably from 40 to 180°C, in particular from 60 to 140°C. The distillation is carried out in such a way that the temperature at the top of the distillation  
10 apparatus is preferably from -15 to 200°C, more preferably from 5 to 150°C, in particular from 10 to 100°C. In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained both at the top and in the bottom of the distillation apparatus.

15 In a particularly preferred embodiment of the present invention, the distillation, carried out in process step (b), of stream 1 takes place under pressure and temperature conditions under which the isomerization catalyst present in the mixture is less active than in process step (a) or is inactive.

20 In a preferred embodiment of the present invention, stream 3, obtained in process step (b), which comprises the at least one isomerization catalyst is recycled at least partly into process step (a).

In a further embodiment of the process according to the invention, process steps (a)  
25 and (b) take place in the same apparatus. It is also possible that stream 3 which comprises the at least one isomerization catalyst is not withdrawn from process step (b) and resides in the common apparatus of process steps (a) and (b).

Alternatively, it is also possible that stream 3, stemming from process step (b), which  
30 comprises the at least one isomerization catalyst is used at least partly to prepare the reactant stream used in accordance with the invention in process step (e). In process step (e), this at least one isomerization catalyst then functions as a hydrocyanation catalyst.

35 *Process step (c)*

In process step (c), a distillation of stream 2 takes place. This gives a stream 4 as the top product which, compared to stream 2, is enriched in (Z)-2-methyl-2-butenitrile in relation to the sum of all pentenenitriles present in stream 2. In addition, a stream 5 is  
40 obtained as the bottom product which, compared to stream 2, is depleted in (Z)-2-methyl-2-butenitrile in relation to the sum of all pentenenitriles present in stream 2.

Process step (c) may be carried out in any suitable apparatus known to those skilled in the art. Suitable apparatus for distillation is described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-cap tray columns, columns  
5 having structured packing or random packing, which may also be operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporating, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensation of the vapor stream. The  
10 distillation can be carried out in a plurality of, such as two or three, apparatuses, advantageously in a single apparatus. The distillation may additionally be effected in one stage in the case of a partial evaporation of the feed stream.

Process step (c) of the process according to the invention is preferably carried out at  
15 an absolute pressure of from 0.1 mbar to 100 bar, more preferably from 1 mbar to 6 bar, in particular from 10 mbar to 500 mbar. The distillation is carried out in such a way that the temperature in the bottom of the distillation apparatus is preferably from 25 to 250°C, more preferably from 40 to 180°C, in particular from 60 to 140°C. The  
20 distillation is carried out in such a way that the temperature at the top of the distillation apparatus is preferably from -15 to 200°C, more preferably from 5 to 150°C, in particular from 10 to 100°C. In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained both at the top and in the bottom of the distillation apparatus.

25 In a particularly preferred embodiment of the process according to the invention, process steps (b) and (c) are carried out together in one distillation apparatus, in which case stream 3 which comprises the at least one isomerization catalyst is obtained as the bottom product, stream 4 which comprises (Z)-2-methyl-2-butenenitrile as the top product, and stream 5 which comprises 3-pentenitrile and 2-methyl-3-butenenitrile at  
30 a side draw of the column.

In a further preferred embodiment of the process according to the invention, process steps (a), (b) and (c) are carried out together in one distillation apparatus. In this case, stream 4 which comprises (Z)-2-methyl-2-butenenitrile is obtained as the top product.  
35 Stream 5 which comprises 3-pentenitrile and 2-methyl-3-butenenitrile is obtained at a side draw of the distillation column. In this embodiment, the isomerization catalyst remains preferably in the bottom of the distillation column.

#### *Process step (d)*

40 Stream 5, obtained in process step (c), which comprises 3-pentenitrile and 2-methyl-3-butenenitrile is subsequently transferred to a further distillation apparatus. In this

distillation apparatus, stream 5 is separated into a 3-pentenitrile stream which is withdrawn as the bottom product, and a 2-methyl-3-butenitrile stream which is withdrawn at the top.

- 5 Process step (d) may be carried out in any suitable apparatus known to those skilled in the art. Suitable apparatus for distillation is described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or random packing, which may also be operated as dividing  
10 wall columns. These distillation units are each equipped with suitable apparatus for evaporating, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensation of the vapor stream. The distillation can be carried out in a plurality of, such as two or three, apparatuses,  
15 advantageously in a single apparatus. The distillation may additionally be effected in one stage in the case of a partial evaporation of the feed stream.

- The absolute pressure in process step (d) is preferably from 0.001 to 100 bar, more preferably from 0.01 to 20 bar, in particular from 0.05 to 2 bar. The distillation is carried  
20 out in such a way that the temperature in the bottom of the distillation apparatus is preferably from 30 to 250°C, more preferably from 50 to 200°C, in particular from 60 to 180°C. The distillation is carried out in such a way that the condensation temperature at the top of the distillation apparatus is preferably from -50 to 250°C, more preferably from 0 to 180°C, in particular from 15 to 160°C.

- 25 In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained both at the top and in the bottom of the distillation apparatus.

- 30 In a particularly preferred embodiment of the process according to the invention, process step (d) and process step (g) are carried out in the same distillation apparatus. In this case, streams 6 and 12, and also 7 and 13, coincide. In addition, in this preferred embodiment, stream 5 is conducted directly into the common apparatus of process steps (d) and (g). In this case, the inlet points of streams 5 and 11, in the case  
35 of a distillation column as the distillation apparatus, may be the same or different.

- In a further embodiment of the process according to the invention, process steps (c) and (g) are carried out in a common distillation column, in which case process step (d) is dispensed with, stream 2 from process step (b) and stream 11 from process step (f)  
40 are conducted into process step (g), and, in process step (g), stream 4 is obtained as the top product comprising (Z)-2-methyl-2-butenitrile, stream 12 as the bottom

product comprising 3-pentenitrile and stream 13 as a side draw stream comprising 2-methyl-3-butenitrile.

5 In the process according to the invention of embodiment I, it is possible that stream 2 is recycled directly into process step (g) and the reactant stream is conducted directly into process step (c), in which case a stream 5a from process step (c) is recycled into the isomerization of process step (a).

10 Alternatively, it is also possible to recycle stream 2 directly into process step (g) and conduct the reactant stream into process step (c), in which case stream 5 from process step (c) is recycled into process step (f).

15 Alternatively, it is also possible that stream 2 is recycled directly into process step (g) and the reactant stream is conducted into process step (c), and stream 5 from process step (c) is recycled into process step (e).

#### Embodiment II

20 The present invention further provides a process for preparing 3-pentenitrile according to an embodiment II, which is characterized by the following process steps:

25 (a') isomerizing a reactant stream which comprises 2-methyl-3-butenitrile over at least one dissolved or dispersed isomerization catalyst to give a stream 1' which comprises 3-pentenitrile, 2-methyl-3-butenitrile, the at least one isomerization catalyst and (Z)-2-methyl-2-butenitrile,

30 (b') distilling stream 1' to obtain a stream 2' which comprises (Z)-2-methyl-2-butenitrile, 2-methyl-3-butenitrile, and recycling it into the isomerization step (a'), a stream 3' as the bottom product which comprises the at least one isomerization catalyst and recycling it into the isomerization step (a'), and a stream 4' which comprises 3-pentenitrile at a side draw of the distillation column.

35 The reactant stream which is used in process step (a') of the process according to the invention according to embodiment II may be obtained by the above-described process for preparing the reactant stream for the process according to the invention according to embodiment I.

40 For process step (a') according to embodiment II, the same conditions apply as for process step (a) according to embodiment I, especially with regard to the catalyst complex used and the free ligand.

The absolute pressure in process step (b') is preferably from 0.001 to 100 bar, more preferably from 0.01 to 20 bar, in particular from 0.1 to 2 bar. The distillation is carried out in such a way that the temperature in the bottom of the distillation apparatus is preferably from 25 to 250°C, more preferably from 40 to 180°C, in particular from 60 to 140°C. The distillation is carried out in such a way that the condensation temperature at the top of the distillation apparatus is preferably from -50 to 250°C, more preferably from 0 to 150°C, in particular from 10 to 100°C.

A partial discharge of stream 2' is in some cases appropriate in order to prevent accumulation of (Z)-2-methyl-2-butenenitrile. The residual stream is recycled in step (a').

In one variant of the present process according to embodiment II, the reactant stream is conducted into process step (b') instead of into process step (a').

Stream 2' which leaves process step (b') in the process according to the invention according to embodiment II may, if appropriate, in a further optional process step (c') be subjected to a distillation. This preferably forms a (Z)-2-methyl-2-butenenitrile-enriched stream 5' and a (Z)-2-methyl-2-butenenitrile-depleted stream 6', and stream 5' is preferably recycled into process step (a').

Process step (c') to be carried out if appropriate may also be carried out in the apparatus of process step (a'), in which case a distillation apparatus is then used in process step (a') in whose bottom the isomerization reaction takes place, stream 1' is drawn off via the bottom of the distillation apparatus, and the (Z)-2-methyl-2-butenenitrile-rich stream 6' is drawn off via the top of the distillation apparatus.

According to the invention, in the processes according to embodiment I and II, 3-pentenitrile is obtained. In the context of the present invention, the term 3-pentenitrile refers to a single isomer of 3-pentenitrile or a mixture of two, three, four or five different such isomers. Isomers include cis-2-pentenitrile, trans-2-pentenitrile, cis-3-pentenitrile, trans-3-pentenitrile, 4-pentenitrile or mixtures thereof, preferably cis-3-pentenitrile, trans-3-pentenitrile, 4-pentenitrile or mixtures thereof, which are referred to in the context of the present invention, both in each case individually and as a mixture, as 3-pentenitrile.

The process according to the invention is associated with advantages. For instance, in an integrated process for preparing adiponitrile, for example, the recycling of unconverted 2-methyl-3-butenenitrile from the isomerization is economically necessary, because the degree of conversion of 2-methyl-3-butenenitrile to 3-pentenitrile is restricted by the thermodynamic equilibrium. The recycling entails the removal of (Z)-2-methyl-2-butenenitrile which accumulates in the 2-methyl-3-butenenitrile circuit. In the process according to the invention, the removal is effected by distillation to separate 2-

methyl-3-butenenitrile and (Z)-2-methyl-2-butenenitrile preferably only after step (a) has been carried out, in step (c), in order to minimize losses of products of value in a controlled manner.

- 5 The process according to the invention according to a preferred version of embodiment I is illustrated in detail with reference to Figure 1:

10 In a reactor R1, hydrogen cyanide and 1,3-butadiene are fed in in the presence of a nickel(0) catalyst. In the reactor, hydrocyanation takes place to form a stream 8. This stream 8 comprises 3-pentenitrile, 2-methyl-3-butenenitrile, the hydrocyanation catalyst and unconverted 1,3-butadiene. Subsequently, stream 8 is transferred to a distillation column K1 in which 1,3-butadiene (stream 9) is removed from stream 8 overhead. In the bottom of the distillation column K1, a stream 10 is obtained which comprises the hydrocyanation catalyst. At the side draw of the distillation column K1, a stream 11 is obtained which comprises 3-pentenitrile and 2-methyl-3-butenenitrile. This stream 11 is subsequently transferred to a distillation column K2.

20 In the distillation column K2, stream 11 is separated into a stream 12 which comprises 3-pentenitrile, and a stream 13 which comprises 2-methyl-3-butenenitrile.

Stream 13 is subsequently transferred to an isomerization apparatus R2. In this isomerization apparatus R2, the 2-methyl-3-butenenitrile which is present in stream 13 is isomerized over an isomerization catalyst. The stream 1 stemming from this isomerization comprises 3-pentenitrile, 2-methyl-3-butenenitrile, (Z)-2-methyl-2-butenenitrile, and also the isomerization catalyst.

25 This stream 1 is subsequently separated in a distillation apparatus K3. This forms stream 3 which comprises the isomerization catalyst (bottoms). At the top of the distillation apparatus K3, stream 2 is withdrawn. This stream 2 comprises 3-pentenitrile, (Z)-2-methyl-2-butenenitrile and 2-methyl-3-butenenitrile. This stream 2 is subsequently transferred to a distillation column K4.

30 In this distillation column K4, stream 2 is separated into (Z)-2-methyl-2-butenenitrile which has been formed during the isomerization (stream 4). In addition, stream 5 is obtained in the bottom of the distillation column K4 and comprises 3-pentenitrile and 2-methyl-3-butenenitrile. This stream 5 is transferred to the distillation column K2, and the 3-pentenitrile is obtained from stream 5 in the distillation column.

40 Streams 9 and 10 may be partly or fully recycled into the reactor R1, or not recycled into it at all. The same applies to stream 3 in the direction of reactor R2. These variants are not shown in Figure 1.

The process according to the invention according to a preferred version of embodiment II is illustrated in detail with reference to Figure 2:

5 In a reactor R1, hydrogen cyanide and 1,3-butadiene are fed in in the presence of a nickel(0) catalyst. In the reactor, hydrocyanation takes place to form a stream 8. This stream 8 comprises 3-pentenitrile, 2-methyl-3-butenitrile, the hydrocyanation catalyst and unconverted 1,3-butadiene. Subsequently, stream 8 is transferred to a distillation column K1 in which 1,3-butadiene (stream 9) is removed from stream 8 overhead. In the bottom of the distillation column K1, a stream 10 is obtained which  
10 comprises the hydrocyanation catalyst. At the side draw of the distillation column K1, a stream 11 is obtained which comprises 3-pentenitrile and 2-methyl-3-butenitrile. This stream 11 is subsequently transferred to an isomerization apparatus R2.

15 In the isomerization apparatus R2, isomerization catalyst (stream 3') and 2-methyl-3-butenitrile (stream 2'), each stemming from the distillation column K2, are additionally introduced. In the isomerization apparatus R2, an isomerization takes place. The stream 1' resulting therefrom is subsequently transferred to the distillation apparatus K2 in which stream 1' is separated into a stream 2' (2-methyl-3-butenitrile) which is recycled into R2, a stream 3' (isomerization catalyst) which is recycled into R2,  
20 and into a stream 4' which comprises 3-pentenitrile.

Feeding of a stream comprising isomerization catalyst to R2 allows any necessary discharges from stream 3' to be compensated, so that the Ni(0) content in R2 remains constant.

25 Streams 9 and 10 may be recycled fully or partly into the reactor R1, or not recycled into it at all.

These recycling and discharge variants are not shown in Figure 2.

30

### Embodiment III

In embodiment III, hydrocyanation and isomerization Ni(0) catalysts of those ligands which catalyze process steps a\*) and e\*) are used.

35

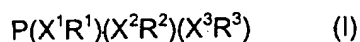
The nickel( $\phi$ ) complexes used with preference as a catalyst, which contain phosphorus ligands and/or free phosphorus ligands, are preferably homogeneously dissolved nickel( $\phi$ ) complexes.

40 The phosphorus ligands of the nickel(0) complexes and the free phosphorus ligands are preferably selected from the group of the mono- or bidentate phosphines, phosphites, phosphinites and phosphonites, preferably of the mono- or bidentate

phosphites, phosphinites and phosphonites, more preferably of the mono- or bidentate phosphites and phosphonites, in particular of the monodentate phosphites, phosphinites and phosphonites, most preferably of the monodentate phosphites and phosphonites.

5

These phosphorus ligands preferably have the formula I



- 10 In the context of the present invention, compound I is a single compound or a mixture of different compounds of the aforementioned formula.

- According to the invention,  $X^1$ ,  $X^2$ ,  $X^3$  each independently are oxygen or a single bond. When all of the  $X^1$ ,  $X^2$  and  $X^3$  groups are single bonds, compound I is a phosphine of the formula  $P(R^1R^2R^3)$  with the definitions of  $R^1$ ,  $R^2$  and  $R^3$  specified in this description.

15

When two of the  $X^1$ ,  $X^2$  and  $X^3$  groups are single bonds and one is oxygen, compound I is a phosphinite of the formula  $P(OR^1)(R^2)(R^3)$  or  $P(R^1)(OR^2)(R^3)$  or  $P(R^1)(R^2)(OR^3)$  with the definitions of  $R^1$ ,  $R^2$  and  $R^3$  specified below.

20

When one of the  $X^1$ ,  $X^2$  and  $X^3$  groups is a single bond and two are oxygen, compound I is a phosphonite of the formula  $P(OR^1)(OR^2)(R^3)$  or  $P(R^1)(OR^2)(OR^3)$  or  $P(OR^1)(R^2)(OR^3)$  with the definitions of  $R^1$ ,  $R^2$  and  $R^3$  specified in this description.

- 25 In one embodiment, all  $X^1$ ,  $X^2$  and  $X^3$  groups should be oxygen, so that compound I is a phosphite of the formula  $P(OR^1)(OR^2)(OR^3)$  with the definitions of  $R^1$ ,  $R^2$  and  $R^3$  specified below.

- According to the invention,  $R^1$ ,  $R^2$ ,  $R^3$  are each independently identical or different organic radicals.  $R^1$ ,  $R^2$  and  $R^3$  are each independently alkyl radicals preferably having from 1 to 10 carbon atoms, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, aryl groups such as phenyl, o-tolyl, m-tolyl, p-tolyl, 1-naphthyl, 2-naphthyl, or hydrocarbyl, preferably having from 1 to 20 carbon atoms, such as 1,1'-biphenol, 1,1'-binaphthol. The  $R^1$ ,  $R^2$  and  $R^3$  groups may be bonded together directly, i.e. not solely via the central phosphorus atom. Preference is given to the  $R^1$ ,  $R^2$  and  $R^3$  groups not being bonded together directly.

35

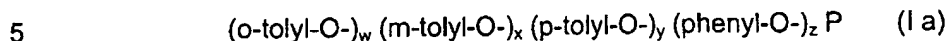
- In one embodiment,  $R^1$ ,  $R^2$  and  $R^3$  groups are radicals selected from the group consisting of phenyl, o-tolyl, m-tolyl and p-tolyl. In one embodiment, a maximum of two of the  $R^1$ ,  $R^2$  and  $R^3$  groups should be phenyl groups.

40

In another embodiment, a maximum of two of the  $R^1$ ,  $R^2$  and  $R^3$  groups should be o-

tolyl groups.

Compounds I which may be used are those of the formula I a



where w, x, y and z are each a natural number and the following conditions apply:  $w + x + y + z = 3$  and  $w, z \leq 2$ .

- 10 Such compounds I a are, for example, (p-tolyl-O-)(phenyl-O-)<sub>2</sub>P, (m-tolyl-O-)(phenyl-O-)<sub>2</sub>P, (o-tolyl-O-)(phenyl-O-)<sub>2</sub>P, (p-tolyl-O-)<sub>2</sub>(phenyl-O-)P, (m-tolyl-O-)<sub>2</sub>(phenyl-O-)P, (o-tolyl-O-)<sub>2</sub>(phenyl-O-)P, (m-tolyl-O-)(p-tolyl-O-)(phenyl-O-)P, (o-tolyl-O-)(p-tolyl-O-)(phenyl-O-)P, (o-tolyl-O-)(m-tolyl-O-)(phenyl-O-)P, (p-tolyl-O-)<sub>3</sub>P, (m-tolyl-O-)(p-tolyl-O-)<sub>2</sub>P, (o-tolyl-O-)(p-tolyl-O-)<sub>2</sub>P, (m-tolyl-O-)<sub>2</sub>(p-tolyl-O-)P, (o-tolyl-O-)<sub>2</sub>(p-tolyl-O-)P, (o-tolyl-O-)(m-tolyl-O-)(p-tolyl-O-)P, (m-tolyl-O-)<sub>3</sub>P, (o-tolyl-O-)(m-tolyl-O-)<sub>2</sub>P (o-tolyl-O-)<sub>2</sub>(m-tolyl-O-)P or mixtures of such compounds.

- 20 Mixtures comprising (m-tolyl-O-)<sub>3</sub>P, (m-tolyl-O-)<sub>2</sub>(p-tolyl-O-)P, (m-tolyl-O-)(p-tolyl-O-)<sub>2</sub>P and (p-tolyl-O-)<sub>3</sub>P may be obtained, for example, by reacting a mixture comprising m-cresol and p-cresol, in particular in a molar ratio of 2:1, as obtained in the distillative workup of crude oil, with a phosphorus trihalide, such as phosphorus trichloride.

- 25 In one embodiment, the phosphorus ligands are the phosphites, described in detail in DE-A 199 53 058, of the formula I b:



- 30 where

- 35  $\text{R}^1$ : aromatic radical having a C<sub>1</sub>-C<sub>18</sub>-alkyl substituent in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system, or having an aromatic substituent in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system, or having a fused aromatic system in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system,

- 40  $\text{R}^2$ : aromatic radical having a C<sub>1</sub>-C<sub>18</sub>-alkyl substituent in the m-position to the oxygen atom which joins the phosphorus atom to the aromatic system, or having an aromatic substituent in the m-position to the oxygen atom which joins the phosphorus atom to the aromatic system, or having a fused aromatic system in

the m-position to the oxygen atom which joins the phosphorus atom to the aromatic system, the aromatic radical bearing a hydrogen atom in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system,

- 5  $R^3$ : aromatic radical having a  $C_1$ - $C_{18}$ -alkyl substituent in the p-position to the oxygen atom which joins the phosphorus atom to the aromatic system, or having an aromatic substituent in the p-position to the oxygen atom which joins the phosphorus atom to the aromatic system, the aromatic radical bearing a hydrogen atom in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system,
- 10
- $R^4$ : aromatic radical which bears substituents other than those defined for  $R^1$ ,  $R^2$  and  $R^3$  in the o-, m- and p-position to the oxygen atom which joins the phosphorus atom to the aromatic system, the aromatic radical bearing a hydrogen atom in the o-position to the oxygen atom which joins the phosphorus atom to the aromatic system,
- 15
- x: 1 or 2,
- 20 y, z, p: each independently 0, 1 or 2, with the proviso that  $x+y+z+p=3$ .

Preferred phosphites of the formula I b can be taken from DE-A 199 53 058. The  $R^1$  radical may advantageously be o-tolyl, o-ethylphenyl, o-n-propylphenyl, o-isopropylphenyl, o-n-butylphenyl, o-sec-butylphenyl, o-tert-butylphenyl, (o-phenyl)phenyl or 1-naphthyl groups.

25

Preferred  $R^2$  radicals are m-tolyl, m-ethylphenyl, m-n-propylphenyl, m-isopropylphenyl, m-n-butylphenyl, m-sec-butylphenyl, m-tert-butylphenyl, (m-phenyl)phenyl or 2-naphthyl groups.

30

Advantageous  $R^3$  radicals are p-tolyl, p-ethylphenyl, p-n-propylphenyl, p-isopropylphenyl, p-n-butylphenyl, p-sec-butylphenyl, p-tert-butylphenyl or (p-phenyl)phenyl groups.

- 35 The  $R^4$  radical is preferably phenyl. p is preferably zero. For the indices x, y, z and p in compound I b, there are the following possibilities:

x	y	z	p
1	0	0	2
1	0	1	1
1	1	0	1
2	0	0	1

1	0	2	0
1	1	1	0
1	2	0	0
2	0	1	0
2	1	0	0

Preferred phosphites of the formula I b are those in which p is zero, and R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each independently selected from o-isopropylphenyl, m-tolyl and p-tolyl, and R<sup>4</sup> is phenyl.

5

Particularly preferred phosphites of the formula I b are those in which R<sup>1</sup> is the o-isopropylphenyl radical, R<sup>2</sup> is the m-tolyl radical and R<sup>3</sup> is the p-tolyl radical with the indices specified in the table above; also those in which R<sup>1</sup> is the o-tolyl radical, R<sup>2</sup> is the m-tolyl radical and R<sup>3</sup> is the p-tolyl radical with the indices specified in the table; additionally those in which R<sup>1</sup> is the 1-naphthyl radical, R<sup>2</sup> is the m-tolyl radical and R<sup>3</sup> is the p-tolyl radical with the indices specified in the table; also those in which R<sup>1</sup> is the o-tolyl radical, R<sup>2</sup> is the 2-naphthyl radical and R<sup>3</sup> is the p-tolyl radical with the indices specified in the table; and finally those in which R<sup>1</sup> is the o-isopropylphenyl radical, R<sup>2</sup> is the 2-naphthyl radical and R<sup>3</sup> is the p-tolyl radical with the indices specified in the table; and also mixtures of these phosphites.

15

Phosphites of the formula I b may be obtained by

- a) reacting a phosphorus trihalide with an alcohol selected from the group consisting of R<sup>1</sup>OH, R<sup>2</sup>OH, R<sup>3</sup>OH and R<sup>4</sup>OH or mixtures thereof to obtain a dihalophosphorous monoester,
- b) reacting the dihalophosphorous monoester mentioned with an alcohol selected from the group consisting of R<sup>1</sup>OH, R<sup>2</sup>OH, R<sup>3</sup>OH and R<sup>4</sup>OH or mixtures thereof to obtain a monohalophosphorous diester and
- c) reacting the monohalophosphorous diester mentioned with an alcohol selected from the group consisting of R<sup>1</sup>OH, R<sup>2</sup>OH, R<sup>3</sup>OH and R<sup>4</sup>OH or mixtures thereof to obtain a phosphite of the formula I b.

30

The reaction may be carried out in three separate steps. Equally, two of the three steps may be combined, i.e. a) with b) or b) with c). Alternatively, all of steps a), b) and c) may be combined together.

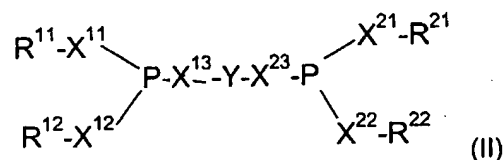
- Suitable parameters and amounts of the alcohols selected from the group consisting of R<sup>1</sup>OH, R<sup>2</sup>OH, R<sup>3</sup>OH and R<sup>4</sup>OH or mixtures thereof may be determined readily by a few simple preliminary experiments.

35

Useful phosphorus trihalides are in principle all phosphorus trihalides, preferably those in which the halide used is Cl, Br, I, in particular Cl, and mixtures thereof. It is also possible to use mixtures of various identically or differently halogen-substituted phosphines as the phosphorus trihalide. Particular preference is given to  $\text{PCl}_3$ . Further details on the reaction conditions in the preparation of the phosphites I b and for the workup can be taken from DE-A 199 53 058.

The phosphites I b may also be used in the form of a mixture of different phosphites I b as a ligand. Such a mixture may be obtained, for example, in the preparation of the phosphites I b.

It is likewise possible for the phosphorus ligand to be multidentate, in particular bidentate. The ligand used then has, for example, the formula II



where

$\text{X}^{11}, \text{X}^{12}, \text{X}^{13}, \text{X}^{21}, \text{X}^{22}, \text{X}^{23}$  are each independently oxygen or a single bond  
 $\text{R}^{11}, \text{R}^{12}$  are each independently identical or different, separate or bridged organic radicals  
 $\text{R}^{21}, \text{R}^{22}$  are each independently identical or different, separate or bridged organic radicals,  
 $\text{Y}$  is a bridging group.

In the context of the present invention, compound II is a single compound or a mixture of different compounds of the aforementioned formula.

In one embodiment,  $\text{X}^{11}, \text{X}^{12}, \text{X}^{13}, \text{X}^{21}, \text{X}^{22}, \text{X}^{23}$  may each be oxygen. In such a case, the bridging group Y is bonded to phosphite groups.

In another embodiment,  $\text{X}^{11}$  and  $\text{X}^{12}$  may each be oxygen and  $\text{X}^{13}$  a single bond, or  $\text{X}^{11}$  and  $\text{X}^{13}$  each oxygen and  $\text{X}^{12}$  a single bond, so that the phosphorus atom surrounded by  $\text{X}^{11}, \text{X}^{12}$  and  $\text{X}^{13}$  is the central atom of a phosphonite. In such a case,  $\text{X}^{21}, \text{X}^{22}$  and  $\text{X}^{23}$  may each be oxygen, or  $\text{X}^{21}$  and  $\text{X}^{22}$  may each be oxygen and  $\text{X}^{23}$  a single bond, or  $\text{X}^{21}$  and  $\text{X}^{23}$  may each be oxygen and  $\text{X}^{22}$  a single bond, or  $\text{X}^{23}$  may be oxygen and  $\text{X}^{21}$  and  $\text{X}^{22}$  each a single bond, or  $\text{X}^{21}$  may be oxygen and  $\text{X}^{22}$  and  $\text{X}^{23}$  each a single bond, or  $\text{X}^{21}, \text{X}^{22}$  and  $\text{X}^{23}$  may each be a single bond, so that the phosphorus atom surrounded by  $\text{X}^{21}, \text{X}^{22}$  and  $\text{X}^{23}$  may be the central atom of a phosphite, phosphonite,

phosphinite or phosphine, preferably a phosphonite.

5 In another embodiment,  $X^{13}$  may be oxygen and  $X^{11}$  and  $X^{12}$  each a single bond, or  $X^{11}$  may be oxygen and  $X^{12}$  and  $X^{13}$  each a single bond, so that the phosphorus atom surrounded by  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  is the central atom of a phosphonite. In such a case,  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be oxygen, or  $X^{23}$  may be oxygen and  $X^{21}$  and  $X^{22}$  each a single bond, or  $X^{21}$  may be oxygen and  $X^{22}$  and  $X^{23}$  each a single bond, or  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may be the central atom of a phosphite, phosphinite or phosphine, preferably a phosphinite.

10 In another embodiment,  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{11}$ ,  $X^{12}$  and  $X^{13}$  is the central atom of a phosphine. In such a case,  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be oxygen, or  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may each be a single bond, so that the phosphorus atom surrounded by  $X^{21}$ ,  $X^{22}$  and  $X^{23}$  may be the central atom of a phosphite or phosphine, preferably a phosphine.

15 The bridging group Y is preferably an aryl group which is substituted, for example by  $C_1$ - $C_4$ -alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or is unsubstituted, preferably a group having from 6 to 20 carbon atoms in the aromatic system, in particular pyrocatechol, bis(phenol) or bis(naphthol).

20 The  $R^{11}$  and  $R^{12}$  radicals may each independently be identical or different organic radicals. Advantageous  $R^{11}$  and  $R^{12}$  radicals are aryl radicals, preferably those having from 6 to 10 carbon atoms, which may be unsubstituted or mono- or polysubstituted, in particular by  $C_1$ - $C_4$ -alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or unsubstituted aryl groups.

30 The  $R^{21}$  and  $R^{22}$  radicals may each independently be the same or different organic radicals. Advantageous  $R^{21}$  and  $R^{22}$  radicals are aryl radicals, preferably those having from 6 to 10 carbon atoms, which may be unsubstituted or mono- or polysubstituted, in particular by  $C_1$ - $C_4$ -alkyl, halogen, such as fluorine, chlorine, bromine, halogenated alkyl, such as trifluoromethyl, aryl, such as phenyl, or unsubstituted aryl groups.

35 The  $R^{11}$  and  $R^{12}$  radicals may each be separate or bridged. The  $R^{21}$  and  $R^{22}$  radicals too may each be separate or bridged. The  $R^{11}$ ,  $R^{12}$ ,  $R^{21}$  and  $R^{22}$  radicals may each be separate, two may be bridged and two separate, or all four may be bridged, in the manner described.

40 In one embodiment, useful compounds are those of the formula I, II, III, IV and V specified in US 5,723,641. In one embodiment, useful compounds are those of the

formula I, II, III, IV, V, VI and VII specified in US 5,512,696, in particular the compounds used there in examples 1 to 31. In one embodiment, useful compounds are those of the formula I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV and XV specified in US 5,821,378, in particular the compounds used there in examples 1 to 73.

5

In one embodiment, useful compounds are those of the formula I, II, III, IV, V and VI specified in US 5,512,695, in particular the compounds used there in examples 1 to 6.

In one embodiment, useful compounds are those of the formula I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII and XIV specified in US 5,981,772, in particular the compounds used there in examples 1 to 66.

10

In one embodiment, useful compounds are those specified in US 6,127,567 and the compounds used there in examples 1 to 29. In one embodiment, useful compounds are those of the formula I, II, III, IV, V, VI, VII, VIII, IX and X specified in US 6,020,516, in particular the compounds used there in examples 1 to 33. In one embodiment, useful compounds are those specified in US 5,959,135 and the compounds used there in examples 1 to 13.

15

In one embodiment, useful compounds are those of the formula I, II and III specified in US 5,847,191. In one embodiment, useful compounds are those specified in US 5,523,453, in particular the compounds illustrated there in formula 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 and 21. In one embodiment, useful compounds are those specified in WO 01/14392, in particular the compounds illustrated there in formula V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV, XV, XVI, XVII, XXI, XXII, XXIII.

20

25

In one embodiment, useful compounds are those specified in WO 98/27054. In one embodiment, useful compounds are those specified in WO 99/13983. In one embodiment, useful compounds are those specified in WO 99/64155.

30

In one embodiment, useful compounds are those specified in the German patent application DE 100 380 37. In one embodiment, useful compounds are those specified in the German patent application DE 100 460 25. In one embodiment, useful compounds are those specified in the German patent application DE 101 502 85.

35

In one embodiment, useful compounds are those specified in the German patent application DE 101 502 86. In one embodiment, useful compounds are those specified in the German patent application DE 102 071 65. In a further embodiment of the present invention, useful phosphorus chelate ligands are those specified in US 2003/0100442 A1.

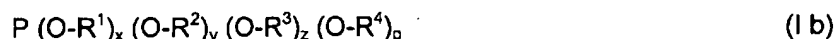
40

In a further embodiment of the present invention, useful phosphorus chelate ligands

are those specified in the German patent application reference number DE 103 50 999.2 of 10.30.2003 which has an earlier priority date but had not been published at the priority date of the present application.

- 5 The compounds I, I a, I b and II described and their preparation are known per se. Phosphorus ligands used may also be a mixture comprising at least two of the compounds I, I a, I b and II.

- 10 In a particularly preferred embodiment of the process according to the invention, the phosphorus ligand of the nickel(0) complex and/or the free phosphorus ligand is selected from the phosphites of the formula I b



- 15 where  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are each independently selected from o-isopropylphenyl, m-tolyl and p-tolyl,  $\text{R}^4$  is phenyl; x is 1 or 2, and y, z, p are each independently 0, 1 or 2, with the proviso that  $x+y+z+p = 3$ ; and mixtures thereof, i.e. mixtures of 2 or more, preferably from 2 to 10, more preferably from 2 to 6, of the compounds of the formula Ib.

20

In one embodiment III, the process is characterized by the following process steps:

- (a\*) isomerizing a reactant stream which comprises 2-methyl-3-butenenitrile over at least one dissolved or dispersed isomerization catalyst to give a stream 1 which  
25 comprises the at least one isomerization catalyst, 2-methyl-3-butenenitrile, 3-pentenitrile and (Z)-2-methyl-2-butenenitrile,
- (b\*) distilling stream 1 to obtain a stream 2 as the top product which comprises 2-methyl-3-butenenitrile, 3-pentenitrile and (Z)-2-methyl-2-butenenitrile, and a  
30 stream 3 as the bottom product which comprises the at least one isomerization catalyst,
- (c\*) distilling stream 2 to obtain a stream 4 as the top product which, compared to stream 2, is enriched in (Z)-2-methyl-2-butenenitrile, based on the sum of all  
35 pentenenitriles in stream 2, and a stream 5 as the bottom product which, compared to stream 2, is enriched in 3-pentenitrile and 2-methyl-3-butenenitrile, based on the sum of all pentenenitriles in stream 2,
- (d\*) distilling stream 5 to obtain a stream 6 as the bottom product which comprises 3-pentenitrile and a stream 7 as the top product which comprises 2-methyl-3-butenenitrile,  
40 butenenitrile,

- (h\*) catalyst regeneration to replenish the nickel(0) content of the substreams 14 from stream 3 and 16 from stream 10 to generate a stream 18,
- (i\*) if appropriate with addition of a diluent F to stream 18 to generate stream 19,
- (j\*) extracting stream 18, if appropriate stream 19, with regard to the catalyst components and/or disruptive component(s) by adding a dinitrile stream 20 and hydrocarbon stream 21 to generate two nonmiscible phases 22 and 23, stream 22 comprising the predominant proportion of the catalyst components and stream 23 the predominant proportion of the disruptive component(s),
- (k\*) distillatively removing the hydrocarbon from the catalyst components from stream 22 to generate a stream 25 which comprises the predominant proportion of the catalyst components and, if appropriate, partly or fully recycling stream 25 into process steps (a\*) or (e\*).

#### *Reactant stream*

In process step (a\*) an isomerization of a reactant stream which comprises 2-methyl-3-butenitrile over at least one isomerization catalyst takes place.

In a particular embodiment of the process according to the invention, the reactant stream is obtainable by the following process steps:

- (e\*) hydrocyanating 1,3-butadiene over at least one hydrocyanation catalyst using hydrogen cyanide to obtain a stream 8 which comprises the at least one hydrocyanation catalyst, 3-pentenitrile, 2-methyl-3-butenitrile, 1,3-butadiene and residues of hydrogen cyanide,
- (f\*) distilling stream 8 once or more than once to obtain a stream 9 which comprises 1,3-butadiene, a stream 10 which comprises the at least one hydrocyanation catalyst, and a stream 11 which comprises 3-pentenitrile and 2-methyl-3-butenitrile,
- (g\*) distilling stream 11 to obtain a stream 12 as the bottom product which comprises 3-pentenitrile, and a stream 13 as the top product which comprises 2-methyl-3-butenitrile.

#### *Process step e\*)*

In process step (e\*), to prepare the reactant stream, a hydrocyanation of 1,3-butadiene initially takes place over at least one hydrocyanation catalyst with hydrogen cyanide to

obtain a stream 8 which comprises the at least one hydrocyanation catalyst, 3-pentenitrile, 2-methyl-3-butenitrile and unconverted 1,3-butadiene.

5 Process step (e\*) may be carried out in any suitable apparatus known to those skilled in the art. Useful apparatus for the reaction is thus customary apparatus, as described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 20, John Wiley & Sons, New York, 1996, pages 1040 to 1055, such as stirred tank reactors, loop reactors, gas circulation reactors, bubble column or tubular reactors, in each case, if appropriate, with apparatus to remove heat of reaction. The reaction may  
10 be carried out in a plurality of, such as two or three, apparatuses.

In a preferred embodiment of the process according to the invention, advantageous reactors have been found to be reactors having backmixing characteristics or batteries of reactors having backmixing characteristics. It has been found that batteries of  
15 reactors having backmixing characteristics which are operated in crossflow mode with regard to the metering of hydrogen cyanide are particularly advantageous.

The hydrocyanation may be carried out in the presence or in the absence of a solvent. When a solvent is used, the solvent should be liquid at the given reaction temperature and the given reaction pressure and inert toward the unsaturated compounds and the  
20 at least one catalyst. In general, the solvents used are hydrocarbons, for example benzene or xylene, or nitriles, for example acetonitrile or benzonitrile. However, preference is given to using a ligand as the solvent.

25 The reaction may be carried out in batchwise mode, continuously or in semibatchwise operation.

The hydrocyanation reaction may be carried out by charging the apparatus with all reactants. However, it is preferred when the apparatus is filled with the catalyst, the  
30 unsaturated organic compound and, if appropriate, the solvent. The gaseous hydrogen cyanide preferably floats over the surface of the reaction mixture or is passed through the reaction mixture. A further procedure for charging the apparatus is the filling of the apparatus with the catalyst, hydrogen cyanide and, if appropriate, the solvent, and slowly metering the unsaturated compound into the reaction mixture. Alternatively, it is  
35 also possible that the reactants are introduced into the reactor and the reaction mixture is brought to the reaction temperature at which the hydrogen cyanide is added to the mixture in liquid form. In addition, the hydrogen cyanide may also be added before heating to reaction temperature. The reaction is carried out under conventional hydrocyanation conditions for temperature, atmosphere, reaction time, etc.

40

Preference is given to carrying out the hydrocyanation continuously in one or more stirred process steps. When a multitude of process steps is used, preference is given

to the process steps being connected in series. In this case, the product is transferred from one process step directly into the next process step. The hydrogen cyanide may be fed directly into the first process step or between the individual process steps.

- 5 When the process according to the invention is carried out in semibatchwise operation, preference is given to initially charging the catalyst components and 1,3-butadiene in the reactor, while hydrogen cyanide is metered into the reaction mixture over the reaction time.
- 10 The reaction is preferably carried out at absolute pressures of from 0.1 to 500 MPa, more preferably from 0.5 to 50 MPa, in particular from 1 to 5 MPa. The reaction is preferably carried out at temperatures of from 273 to 473 K, more preferably from 313 to 423 K, in particular from 333 to 393 K. Advantageous average mean residence times of the liquid reactor phase have been found to be in the range from 0.001 to 100 hours,
- 15 preferably from 0.05 to 20 hours, more preferably from 0.1 to 5 hours, in each case per reactor.

In one embodiment, the reaction may be performed in the liquid phase in the presence of a gas phase and, if appropriate, of a solid suspended phase. The starting materials,

20 hydrogen cyanide and 1,3-butadiene, may each be metered in in liquid or gaseous form.

In a further embodiment, the reaction may be carried out in liquid phase, in which case the pressure in the reactor is such that all feedstocks such as 1,3-butadiene, hydrogen

25 cyanide and the at least one catalyst are metered in in liquid form and are in the liquid phase in the reaction mixture. A solid suspended phase may be present in the reaction mixture and may also be metered in together with the at least one catalyst, for example consisting of degradation products of the catalyst system comprising nickel(II) compounds inter alia.

30 In process step (e\*), a stream 8 which comprises 3-pentenitrile, 2-methyl-3-butenitrile, the at least one catalyst and unconverted 1,3-butadiene is obtained.

Process step (f\*)

35 Stream 8 which comprises 3-pentenitrile, 2-methyl-3-butenitrile, the at least one catalyst and unconverted 1,3-butadiene is subsequently transferred in process step (f\*) to a distillation apparatus. In this distillation apparatus, stream 8 is distilled once or more than once to obtain a stream 9 which comprises 1,3-butadiene, a stream 10

40 which comprises the at least one hydrocyanation catalyst, and a stream 11 which comprises 3-pentenitrile and 2-methyl-3-butenitrile.

The distillation of process step (f\*) may be effected in two stages, as described in DE-A-102 004 004 720, process steps (b\*) and (c\*). The distillation of process step (f\*) may also be effected according to DE-A-102 004 004 729, process steps (b\*) and (c\*).

- 5 The distillation(s) of process step (f\*) may be carried out in any suitable apparatus known to those skilled in the art. Suitable apparatus for distillation is described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or random packing, which may  
10 also be operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporating, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensation of the vapor stream. The individual distillations can each be carried out in a plurality of, such  
15 as two or three, apparatuses, advantageously in a single apparatus in each case.

The distillation(s) may additionally each be effected in one stage in the case of a partial evaporation of the feed stream.

- 20 The pressure in process step (f\*) is preferably from 0.001 to 10 bar, more preferably from 0.010 to 1 bar, in particular from 0.02 to 0.5 bar. The distillation(s) is/are carried out in such a way that the temperature(s) in the bottom of the distillation apparatus(es) is/are preferably from 30 to 200°C, more preferably from 50 to 150°C, in particular from 60 to 120°C. The distillation(s) is/are carried out in such a way that the condensation  
25 temperatures at the top of the distillation apparatus are preferably from -50 to 150°C, more preferably from -15 to 60°C, in particular from 5 to 45°C. In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained both at the top and in the bottom of the distillation apparatus(es).

- 30 Stream 11 is subsequently subjected to a distillation in a further process step (g\*). This distillation may be carried out in any suitable apparatus known to those skilled in the art. Suitable apparatus for distillation is described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York,  
35 1996, pages 334-348, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or random packing, which may also be operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporating, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash  
40 evaporators, and also with apparatus for condensation of the vapor stream. The distillation can be carried out in a plurality of, such as two or three, apparatuses,

advantageously in a single apparatus. The distillation may additionally be effected in one stage in the case of a partial evaporation of the feed stream.

- 5 The pressure in process step (g\*) is preferably from 0.001 to 100 bar, more preferably from 0.01 to 20 bar, in particular from 0.05 to 2 bar. The distillation is carried out in such a way that the temperature in the bottom of the distillation apparatus is preferably from 30 to 250°C, more preferably from 50 to 200°C, in particular from 60 to 180°C. The distillation is carried out in such a way that the condensation temperature at the top of the distillation apparatus is preferably from -50 to 250°C, more preferably from 0 to 180°C, in particular from 15 to 160°C. In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained both at the top and in the bottom of the distillation apparatus.

- 15 In process step (g\*), a stream 12 is obtained as the bottom product which comprises 1,3-pentenenitrile, and stream 13 as the top product which comprises 2-methyl-3-butenitrile. Stream 13 is preferably used as the reactant stream in the process according to the invention for preparing 3-pentenenitrile.

- 20 In a further embodiment of the present invention, it is possible that the reactant stream used in the inventive process step (a\*) corresponds to stream 11 of process step (f\*), so that a separation of stream 11 in process step (g\*) is dispensed with.

#### *Process step (a\*)*

- 25 In process step (a\*), an isomerization of the reactant stream which comprises 2-methyl-3-butenitrile takes place over at least one isomerization catalyst. This gives a stream 1 which comprises the isomerization catalyst, unconverted 2-methyl-3-butenitrile, 3-pentenenitrile and (Z)-2-methyl-2-butenitrile.
- 30 According to the invention, the isomerization is carried out in the presence of a system comprising
- nickel(0) and
  - a compound which contains trivalent phosphorus and complexes nickel(0) as a
- 35 ligand.

Nickel(0)-containing catalyst systems can be prepared by processes known per se.

- 40 The ligands for the isomerization catalyst may be the same phosphorus ligands as used for the hydrocyanation catalyst used in process step (e\*). The hydrocyanation catalyst is thus identical to the isomerization catalyst.

The catalyst in process steps (a\*) and (e\*) is substantially Lewis acid-free, i.e. no Lewis acid is added to the catalyst at any time, and the catalyst preferably does not contain any Lewis acid.

- 5 Lewis acid refers in this context to inorganic or organic metal compounds in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include  $\text{ZnBr}_2$ ,  $\text{ZnI}_2$ ,  $\text{ZnCl}_2$ ,  $\text{ZnSO}_4$ ,  $\text{CuCl}_2$ ,  $\text{CuCl}$ ,  $\text{Cu}(\text{O}_3\text{SCF}_3)_2$ ,  $\text{CoCl}_2$ ,  $\text{CoI}_2$ ,  $\text{FeI}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ ,  $\text{FeCl}_2(\text{THF})_2$ ,  
 10  $\text{TiCl}_4(\text{THF})_2$ ,  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{ClTi}(\text{O}-i\text{-propyl})_3$ ,  $\text{MnCl}_2$ ,  $\text{ScCl}_3$ ,  $\text{AlCl}_3$ ,  $(\text{C}_8\text{H}_{17})\text{AlCl}_2$ ,  $(\text{C}_8\text{H}_{17})_2\text{AlCl}$ ,  $(i\text{-C}_4\text{H}_9)_2\text{AlCl}$ ,  $(\text{C}_6\text{H}_5)_2\text{AlCl}$ ,  $(\text{C}_6\text{H}_5)\text{AlCl}_2$ ,  $\text{ReCl}_5$ ,  $\text{ZrCl}_4$ ,  $\text{NbCl}_5$ ,  $\text{VCl}_3$ ,  $\text{CrCl}_2$ ,  $\text{MoCl}_5$ ,  $\text{YCl}_3$ ,  $\text{CdCl}_2$ ,  $\text{LaCl}_3$ ,  $\text{Er}(\text{O}_3\text{SCF}_3)_3$ ,  $\text{Yb}(\text{O}_2\text{CCF}_3)_3$ ,  $\text{SmCl}_3$ ,  $\text{B}(\text{C}_6\text{H}_5)_3$ ,  $\text{TaCl}_5$ ,  $\text{RAlCl}_2$ ,  $\text{R}_2\text{AlCl}$ ,  $\text{R}_3\text{SnO}_3\text{SCF}_3$  and  $\text{R}_3\text{B}$ , where R is an alkyl or aryl group,  $\text{B}(\text{C}_6\text{H}_5)_3$  and  $(\text{C}_6\text{H}_5)_3\text{SnX}$ , where  $\text{X}=\text{CF}_3\text{SO}_3$ ,  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3$  or  $(\text{C}_6\text{H}_5)_3\text{BCN}$ , as described, for  
 15 example, in US 6,127,567, US 6,171,996, US 6,380,421, US 3,496,217, US 3,496,218, US 4,774,353, US 3,773,809, US 3,496,217 and US 4,874,884.

The isomerization may be carried out in the presence of a liquid diluent,

- for example a hydrocarbon such as hexane, heptane, octane, cyclohexane,  
 20 methylcyclohexane, benzene, decahydronaphthalene
- for example an ether such as diethyl ether, tetrahydrofuran, dioxane, glycol dimethyl ether, anisole,
- for example an ester such as ethyl acetate, methyl benzoate, or
- for example a nitrile such as acetonitrile, benzonitrile, or
- 25 - mixtures of such diluents.

In a particularly preferred embodiment, a useful isomerization is in the absence of such a liquid diluent.

- 30 Moreover, it has been found to be advantageous when the isomerization in process step (a\*) is carried out in a nonoxidizing atmosphere, for example under a protective gas atmosphere composed of nitrogen or a noble gas such as argon.

- Process step (a\*) may be carried out in any suitable apparatus known to those skilled  
 35 in the art. Useful apparatus for the reaction is customary apparatus for this purpose, as described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 20, John Wiley & Sons, New York, 1996, pages 1040 to 1055, such as stirred tank reactors, loop reactors, gas circulation reactors, bubble column reactors or tubular reactors. The reaction may be carried out in a plurality of, such as two or three,  
 40 apparatuses.

In a preferred embodiment of the process according to the invention, the isomerization is carried out in a compartmented tubular reactor.

5 In a further preferred embodiment of the process according to the invention, the isomerization is carried out in at least two reactors connected in series, in which case the first reactor has substantially stirred tank characteristics and the second reactor is designed in such a way that it has substantially tubular characteristics.

10 In a particularly preferred embodiment of the process according to the invention, the isomerization is carried out in a reactor, the reactor having the characteristics of a stirred tank battery which corresponds to from 2 to 20 stirred tanks, in particular from 3 to 10 stirred tanks.

15 In one embodiment of the process according to the invention, the reaction may be carried out in one distillation apparatus, in which case the isomerization reaction takes place at least in the bottom region of the distillation apparatus. Any distillation apparatus known to those skilled in the art is suitable, as described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-cap tray  
20 columns, columns having structured packing or random packing, which may also be operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporation, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensing the vapor  
25 stream. The distillation with simultaneous reaction can be carried out in a plurality of, such as two or three, apparatuses, advantageously in a single apparatus. The distillation may additionally be effected in one stage in the case of a partial evaporation of the feed stream.

30 Process step (a\*) of the process according to the invention is preferably carried out at an absolute pressure of from 0.1 mbar to 100 bar, more preferably from 1 mbar to 16 bar, in particular from 10 mbar to 6 bar. The temperature in process step (a\*) is preferably from 25 to 250°C, more preferably from 30 to 180°C, in particular from 40 to 140°C.

35

The composition of the stream withdrawn, with regard to the molar ratio of 2-methyl-3-butenitrile to linear pentenenitrile and thus the degree of conversion of 2-methyl-3-butenitrile used, may be adjusted, depending on the composition of the feed stream, in a technically simple manner by the temperature, the catalyst concentration, the  
40 residence time and the configuration of the reactor. In a preferred embodiment of the process according to the invention, the degree of conversion is adjusted with the aid of

these measures to values in the range from 10 to 99%, more preferably from 30 to 95%, in particular from 60 to 90%.

*Process step (b\*)*

5

In process step (b\*), the stream 1 obtained in process step (a\*) is distilled. This gives a stream 2 which comprises 2-methyl-3-butenitrile, 3-pentenitrile and (Z)-2-methyl-2-butenitrile as the top product. In addition, a stream 3 is obtained in process step (b\*) as the bottom product which comprises the at least one isomerization catalyst.

10

Process step (b\*) of the process according to the invention may be carried out in any suitable distillation apparatus known to those skilled in the art. Suitable apparatus for distillation is described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or random packing, which may also be operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporating, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensation of the vapor stream. The distillation can be carried out in a plurality of, such as two or three, apparatuses, advantageously in a single apparatus. The distillation may additionally be effected in one stage in the case of a partial evaporation of the feed stream.

25

Process step (b\*) of the process according to the invention is preferably carried out at an absolute pressure of from 0.1 mbar to 100 bar, more preferably from 1 mbar to 6 bar, in particular from 10 mbar to 500 mbar. The distillation is carried out in such a way that the temperature in the bottom of the distillation apparatus is preferably from 25 to 250°C, more preferably from 40 to 180°C, in particular from 60 to 140°C. The distillation is carried out in such a way that the temperature at the top of the distillation apparatus is preferably from -15 to 200°C, more preferably from 5 to 150°C, in particular from 10 to 100°C. In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained both at the top and in the bottom of the distillation apparatus.

35

In a particularly preferred embodiment of the present invention, the distillation, carried out in process step (b\*), of stream 1 takes place under pressure and temperature conditions under which the isomerization catalyst present in the mixture is less active than in process step (a\*) or is inactive.

40

In a preferred embodiment of the present invention, stream 3, obtained in process step (b\*), which comprises the at least one isomerization catalyst is recycled at least partly into process step (a\*).

- 5 In a further embodiment of the process according to the invention, process steps (a\*) and (b\*) take place in the same apparatus. It is also possible that stream 3 which comprises the at least one isomerization catalyst is not withdrawn from process step (b\*) and resides in the common apparatus of process steps (a\*) and (b\*).

10 *Process step (c\*)*

- In process step (c\*), a distillation of stream 2 takes place. This gives a stream 4 as the top product which, compared to stream 2, is enriched in (Z)-2-methyl-2-butenenitrile in relation to the sum of all pentenenitriles present in stream 2. In addition, a stream 5 is  
15 obtained as the bottom product which, compared to stream 2, is depleted in (Z)-2-methyl-2-butenenitrile in relation to the sum of all pentenenitriles present in stream 2.

- Process step (c\*) may be carried out in any suitable apparatus known to those skilled in the art. Suitable apparatus for distillation is described, for example, in: Kirk-Othmer,  
20 Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or random packing, which may also be operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporating, such as falling-film evaporators, thin-film evaporators, multiphase helical-  
25 tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensation of the vapor stream. The distillation can be carried out in a plurality of, such as two or three, apparatuses, advantageously in a single apparatus. The distillation may additionally be effected in one stage in the case of a partial evaporation of the feed stream.

- 30 Process step (c\*) of the process according to the invention is preferably carried out at an absolute pressure of from 0.1 mbar to 100 bar, more preferably from 1 mbar to 6 bar, in particular from 10 mbar to 500 mbar. The distillation is carried out in such a way that the temperature in the bottom of the distillation apparatus is preferably from  
35 25 to 250°C, more preferably from 40 to 180°C, in particular from 60 to 140°C. The distillation is carried out in such a way that the temperature at the top of the distillation apparatus is preferably from -15 to 200°C, more preferably from 5 to 150°C, in particular from 10 to 100°C. In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained  
40 both at the top and in the bottom of the distillation apparatus.

In a particularly preferred embodiment of the process according to the invention, process steps (b\*) and (c\*) are carried out together in one distillation apparatus, in which case stream 3 which comprises the at least one isomerization catalyst is obtained as the bottom product, stream 4 which comprises (Z)-2-methyl-2-butenenitrile as the top product, and stream 5 which comprises 3-pentenitrile and 2-methyl-3-butenenitrile at a side draw of the column.

In a further preferred embodiment of the process according to the invention, process steps (a\*), (b\*) and (c\*) are carried out together in one distillation apparatus. In this case, stream 4 which comprises (Z)-2-methyl-2-butenenitrile is obtained as the top product. Stream 5 which comprises 3-pentenitrile and 2-methyl-3-butenenitrile is obtained at a side draw of the distillation column. In this embodiment, the isomerization catalyst remains preferably in the bottom of the distillation column.

15 *Process step (d\*)*

Stream 5, obtained in process step (c\*), which comprises 3-pentenitrile and 2-methyl-3-butenenitrile is subsequently transferred to a further distillation apparatus. In this distillation apparatus, stream 5 is separated into a 3-pentenitrile stream which is withdrawn as the bottom product, and a 2-methyl-3-butenenitrile stream which is withdrawn at the top.

Process step (d\*) may be carried out in any suitable apparatus known to those skilled in the art. Suitable apparatus for distillation is described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 4th ed., Vol. 8, John Wiley & Sons, New York, 1996, pages 334-348, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or random packing, which may also be operated as dividing wall columns. These distillation units are each equipped with suitable apparatus for evaporating, such as falling-film evaporators, thin-film evaporators, multiphase helical-tube evaporators, natural-circulation evaporators or forced-circulation flash evaporators, and also with apparatus for condensation of the vapor stream. The distillation can be carried out in a plurality of, such as two or three, apparatuses, advantageously in a single apparatus. The distillation may additionally be effected in one stage in the case of a partial evaporation of the feed stream.

The absolute pressure in process step (d\*) is preferably from 0.001 to 100 bar, more preferably from 0.01 to 20 bar, in particular from 0.05 to 2 bar. The distillation is carried out in such a way that the temperature in the bottom of the distillation apparatus is preferably from 30 to 250°C, more preferably from 50 to 200°C, in particular from 60 to 180°C. The distillation is carried out in such a way that the condensation temperature at the top of the distillation apparatus is preferably from -50 to 250°C, more preferably from 0 to 180°C, in particular from 15 to 160°C.

In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained both at the top and in the bottom of the distillation apparatus.

5

In a particularly preferred embodiment of the process according to the invention, process step (d\*) and process step (g\*) are carried out in the same distillation apparatus. In this case, streams 6 and 12, and also 7 and 13, coincide. In addition, in this preferred embodiment, stream 5 is conducted directly into the common apparatus of process steps (d\*) and (g\*). In this case, the inlet points of streams 5 and 11, in the case of a distillation column as the distillation apparatus, may be the same or different.

10

In a further embodiment of the process according to the invention, process steps (c\*) and (g\*) are carried out in a common distillation column, in which case process step (d\*) is dispensed with, stream 2 from process step (b\*) and stream 11 from process step (f\*) are conducted into process step (g\*), and, in process step (g\*), stream 4 is obtained as the top product comprising (Z)-2-methyl-2-butenenitrile, stream 12 as the bottom product comprising 3-pentenitrile and stream 13 as a side draw stream comprising 2-methyl-3-butenenitrile.

15

20

In the process according to the invention of embodiment III, it is possible that stream 2 is recycled directly into process step (g\*) and the reactant stream is conducted directly into process step (c\*), in which case a stream 5a from process step (c\*) is recycled into the isomerization of process step (a\*).

25

Alternatively, it is also possible to recycle stream 2 directly into process step (g\*) and conduct the reactant stream into process step (c\*), in which case stream 5 from process step (c\*) is recycled into process step (f\*).

30

Alternatively, it is also possible that stream 2 is recycled directly into process step (g\*) and the reactant stream is conducted into process step (c\*), and stream 5 from process step (c\*) is recycled into process step (e\*).

*Process step h\*):*

35

Process step h\*) comprises a process for preparing nickel(0)-phosphorus ligand complexes containing at least one nickel(0) central atom and at least one phosphorus ligand.

40

In the following, the terms reductive catalyst synthesis/regeneration and redox catalyst synthesis/regeneration are synonymous.

*Process step h<sub>1</sub><sup>\*</sup>):*

- In a preferred embodiment of process step h<sup>\*</sup>), referred to here as process step h<sub>1</sub><sup>\*</sup>), an aqueous nickel(II) halide dried by azeotropic distillation (previously aqueous but of course dry after azeotropic distillation) is reduced in the presence of at least one phosphorus ligand.

*Azeotropic distillation*

- 10 In the azeotropic distillation, an aqueous nickel(II) halide is used. Aqueous nickel(II) halide is a nickel halide which is selected from the group of nickel chloride, nickel bromide and nickel iodide which contains at least 2% by weight of water. Examples thereof are nickel chloride dihydrate, nickel chloride hexahydrate, an aqueous solution of nickel chloride, nickel bromide trihydrate, an aqueous solution of nickel bromide,
- 15 nickel iodide hydrates or an aqueous solution of nickel iodide. In the case of nickel chloride, preference is given to using nickel chloride hexahydrate or an aqueous solution of nickel chloride. In the case of nickel bromide and nickel iodide, preference is given to using the aqueous solutions. Particular preference is given to an aqueous solution of nickel chloride.
- 20 In the case of an aqueous solution, the concentration of the nickel(II) halide in water is not critical per se. An advantageous proportion of the nickel(II) halide in the total weight of nickel(II) halide and water has been found to be at least 0.01% by weight, preferably at least 0.1% by weight, more preferably at least 0.25% by weight, especially preferably
- 25 at least 0.5% by weight. An advantageous proportion of the nickel(II) halide in the total weight of nickel(II) halide and water has been found to be in the region of at most 80% by weight, preferably at most 60% by weight, more preferably at most 40% by weight. For practical reasons, it is advantageous not to exceed a proportion of nickel halide in the mixture of nickel halide and water which results in a solution under the given
- 30 temperature and pressure conditions. In the case of an aqueous solution of nickel chloride, it is therefore advantageous for practical reasons to select at room temperature a proportion of nickel halide in the total weight of nickel chloride and water of at most 31% % by weight. At higher temperatures, higher concentrations may correspondingly be selected which result from the solubility of nickel chloride in water.
- 35 The aqueous nickel(II) halide is dried before the reduction by an azeotropic distillation. In a preferred embodiment of the present invention, the azeotropic distillation is a process for removing water from the corresponding aqueous nickel(II) halide, in which it is admixed with a diluent whose boiling point, in the case that the diluent does not
- 40 form an azeotrope with water, under the pressure conditions of the distillation mentioned below, is higher than the boiling point of water and which is present in liquid form at this boiling point of water or which forms an azeotrope or heteroazeotrope with

water under the pressure and temperature conditions of the distillation mentioned below, and the mixture comprising the aqueous nickel(II) halide and the diluent is distilled to remove water or the azeotrope mentioned or the heteroazeotrope mentioned from this mixture to obtain an aqueous mixture comprising nickel(II) halide and said  
5 diluent.

In addition to the aqueous nickel(II) halide, the starting mixture may comprise further constituents such as ionic or nonionic, organic or inorganic compounds, especially those which are homogeneously and monophasically miscible with the starting mixture  
10 or are soluble in the starting mixture.

According to the invention, the aqueous nickel(II) halide is admixed with a diluent whose boiling point under the pressure conditions of the distillation is higher than the boiling point of water and which is liquid at this boiling point of water.  
15

The pressure conditions for the subsequent distillation are not critical per se. Advantageous pressures have been found to be at least  $10^{-4}$  MPa, preferably at least  $10^{-3}$  MPa, in particular at least  $5 \cdot 10^{-3}$  MPa. Advantageous pressures have been found to be at most 1 MPa, preferably at most  $5 \cdot 10^{-1}$  MPa, in particular at most  $1.5 \cdot 10^{-1}$  MPa.  
20

Depending on the pressure conditions and the composition of the mixture to be distilled, the distillation temperature is then established. At this temperature, the diluent is preferably in liquid form. In the context of the present invention, the term diluent refers either to an individual diluent or to a mixture of diluents, in which case the  
25 physical properties mentioned in the present invention relate to such a mixture.

In addition, the diluent preferably has a boiling point under these pressure and temperature conditions which, in the case that the diluent does not form an azeotrope with water, is higher than that of water, preferably by at least  $5^{\circ}\text{C}$ , in particular at least  $20^{\circ}\text{C}$ , and preferably at most  $200^{\circ}\text{C}$ , in particular at most  $100^{\circ}\text{C}$ .  
30

In a preferred embodiment, diluents may be used which form an azeotrope or heteroazeotrope with water. The amount of diluent compared to the amount of water in the mixture is not critical per se. Advantageously, more liquid diluent should be used  
35 than corresponds to the amounts to be distilled off by the azeotropes, so that excess diluent remains as the bottom product.

When a diluent is used which does not form an azeotrope with water, the amount of diluent compared to the amount of water in the mixture is not critical per se.  
40

The diluent used is selected in particular from the group consisting of organic nitriles, aromatic hydrocarbons, aliphatic hydrocarbons and mixtures of the aforementioned

solvents. With regard to the organic nitriles, preference is given to using acetonitrile, propionitrile, n-butyronitrile, n-valeronitrile, cyanocyclopropane, acrylonitrile, crotonitrile, allyl cyanide, cis-2-pentenitrile, trans-2-pentenitrile, cis-3-pentenitrile, trans-3-pentenitrile, 4-pentenitrile, 2-methyl-3-butenitrile, Z-2-methyl-2-butenitrile, E-2-methyl-2-butenitrile, ethylsuccinonitrile, adiponitrile, methylglutaronitrile or mixtures thereof. With regard to the aromatic hydrocarbons, benzene, toluene, o-xylene, m-xylene, p-xylene or mixtures thereof may preferably be used. Aliphatic hydrocarbons may preferably be selected from the group of the linear or branched aliphatic hydrocarbons, more preferably from the group of the cycloaliphatics, such as cyclohexane or methylcyclohexane, or mixtures thereof. Particular preference is given to using cis-3-pentenitrile, trans-3-pentenitrile, adiponitrile, methylglutaronitrile or mixtures thereof as the solvent.

When the diluent used is an organic nitrile or mixtures comprising at least one organic nitrile, it has been found to be advantageous to select the amount of diluent in such a way that the proportion of nickel(II) halide in the total weight of nickel(II) halide and diluent in the finished mixture is at least 0.05% by weight, preferably at least 0.5% by weight, more preferably at least 1% by weight.

When the diluent used is an organic nitrile or mixtures comprising at least one organic nitrile, it has been found to be advantageous to select the amount of diluent in such a way that the proportion of nickel(II) halide in the total weight of nickel(II) halide and diluent in the finished mixture is at most 50% by weight, preferably at most 30% by weight, more preferably at most 20% by weight.

According to the invention, the mixture comprising the aqueous nickel(II) halide and the diluent is distilled to remove water from this mixture to obtain an anhydrous mixture comprising nickel(II) halide and said diluent. In a preferred embodiment, the mixture is initially prepared and subsequently distilled. In another preferred embodiment, the aqueous nickel halide, more preferably the aqueous solution of the nickel halide, is added gradually to the boiling diluent during the distillation. This allows the formation of a greasy solid which is difficult to handle from a process technology point of view to be substantially prevented.

In the case of pentenenitrile as the diluent, the distillation can advantageously at a pressure of at most 1 megapascal, preferably 0.5 megapascal.

In the case of pentenenitrile as diluent, the distillation can be carried out preferably at a pressure of at least 1 kPa, preferably at least 5 kPa, more preferably at least 10 kPa.

The distillation may advantageously be effected by single-stage evaporation, preferably by fractional distillation in one or more, such as 2 or 3, distillation apparatuses. Useful

apparatus for the distillation is customary apparatus for this purpose, as described, for example, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., Vol. 7, John Wiley & Sons, New York, 1979, pages 870-881, such as sieve tray columns, bubble-cap tray columns, columns having structured packing or random packing, columns  
5 having side draws or dividing wall columns.

The distillation may be carried out batchwise or continuously.

#### Reduction

10

The process for preparing nickel(0) phosphorus ligand complexes containing at least one nickel(0) central atom and at least one phosphorus ligand by reduction is preferably carried out in the presence of a solvent. The solvent is in particular selected from the group consisting of organic nitriles, aromatic hydrocarbons, aliphatic  
15 hydrocarbons and mixtures of the aforementioned solvents. With regard to the organic nitriles, preference is given to using acetonitrile, propionitrile, n-butyronitrile, n-valeronitrile, cyanocyclopropane, acrylonitrile, crotonitrile, allyl cyanide, cis-2-pentenitrile, trans-2-pentenitrile, cis-3-pentenitrile, trans-3-pentenitrile, 4-pentenitrile, 2-methyl-3-butenitrile, Z-2-methyl-2-butenitrile, E-2-methyl-2-  
20 butenitrile, ethylsuccinonitrile, adiponitrile, methylglutaronitrile or mixtures thereof. With regard to the aromatic hydrocarbons, benzene, toluene, o-xylene, m-xylene, p-xylene or mixtures thereof may preferably be used. Aliphatic hydrocarbons may preferably be selected from the group of the linear or branched aliphatic hydrocarbons, more preferably from the group of the cycloaliphatics such as cyclohexane or  
25 methylcyclohexane, or mixtures thereof. Particular preference is given to using cis-3-pentenitrile, trans-3-pentenitrile, adiponitrile, methylglutaronitrile or mixtures thereof as a solvent.

Preference is given to using an inert solvent.

30

The concentration of the solvent is preferably from 10 to 90% by mass, more preferably from 20 to 70% by mass, in particular from 30 to 60% by mass, based in each case on the finished reaction mixture.

35 In a particular embodiment of the present invention, the solvent is identical to the diluent which is used in the above-described inventive process for preparing the anhydrous mixture comprising the nickel(II) halide and the diluent.

40 In the process according to the invention, the concentration of the ligand in the solvent is preferably from 1 to 90% by weight, more preferably from 5 to 80% by weight, in particular from 50 to 80% by weight.

The reducing agent used in the process according to the invention is preferably selected from the group consisting of metals which are more electropositive than nickel, metal alkyls, electrical current, complex hydrides and hydrogen.

- 5 When the reducing agent used in the process according to the invention is a metal which is more electropositive than nickel, this metal is preferably selected from the group consisting of sodium, lithium, potassium, magnesium, calcium, barium, strontium, titanium, vanadium, iron, cobalt, copper, zinc, cadmium, aluminum, gallium, indium, tin, lead and thorium. Particular preference is given in this context to iron and  
10 zinc. When the reducing agent used is aluminum, it is advantageous when it is preactivated by reaction with a catalytic amount of mercury(II) salt or metal alkyl. For the preactivation, preference is given to using triethylaluminum in an amount of preferably from 0.05 to 50 mol%, more preferably from 0.5 to 10 mol%. The reduction metal is preferably finely divided, the term "finely divided" a meaning that the metal is  
15 used in a particle size of less than 10 mesh, more preferably less than 20 mesh.

When the reducing agent used in the process according to the invention is a metal which is more electropositive than nickel, the amount of metal is preferably from 0.1 to 50% by weight, based on the reaction mixture.

- 20 When the reducing agent used in the process according to the invention comprises metal alkyls, they are preferably lithium alkyls, sodium alkyls, magnesium alkyls, in particular Grignard reagents, zinc alkyls or aluminum alkyls. Particular preference is given to aluminum alkyls such as trimethylaluminum, triethylaluminum,  
25 triisopropylaluminum or mixtures thereof, in particular triethylaluminum. The metal alkyls may be used in substance or dissolved in an inert organic solvent such as hexane, heptane or toluene.

- When the reducing agent used in the process according to the invention comprises  
30 complex hydrides, preference is given to using metal aluminum hydrides such as lithium aluminum hydride, or metal borohydrides such as sodium borohydride.

- The molar ratio of the redox equivalents between the nickel(II) source and the reducing agent is preferably from 1 : 1 to 1 : 100, more preferably from 1 : 1 to 1 : 50, in  
35 particular from 1 : 1 to 1 : 5.

- In the process according to the invention, the ligand to be used may also be present in a ligand solution which has already been used as a catalyst solution in hydrocyanation reactions, for example step e\*), or isomerization reactions, for example step a\*), and  
40 has been depleted in nickel(0). Such streams are streams 3 and 10 respectively, either partly or in each case independently selected substreams 14 (from substream 3) and substream 16 (from substream 10) respectively in stage h\*) and the following stages, if

appropriate i\*), j\*) and k\*) conducted are. Any remaining substreams 15 (from stream 3) and 17 (from stream 10) are not conducted through h\*), i\*), j\*) and k\*), but rather recycled directly into stage a\*) or e\*). This "return catalyst solution" generally has the following composition:

- 5
- from 2 to 60% by weight, in particular from 10 to 40% by weight, of pentenenitriles,
  - from 0 to 60% by weight, in particular from 0 to 40% by weight, of adiponitrile,
  - 10 - from 0 to 10% by weight, in particular from 0 to 5% by weight, of other nitriles,
  - from 10 to 90% by weight, in particular from 50 to 90% by weight of phosphorus ligand and
  - 15 - from 0 to 2% by weight, in particular from 0 to 1% by weight, of nickel(0).

The free ligand present in the return catalyst solution may thus be converted again to a nickel(0) complex in the process according to the invention.

- 20 In a particular embodiment of the present invention, the ratio of the nickel(II) source to phosphorus ligand is from 1 : 1 to 1 : 100. Further preferred ratios of nickel(II) source to phosphorus ligand are from 1 : 1 to 1 : 3, in particular from 1 : 1 to 1 : 2.

- 25 The process according to the invention may be carried out at any pressure. For practical reasons, preference is given to pressures between 0.1 bara and 5 bara, preferably 0.5 bara and 1.5 bara.

- The process according to the invention may be carried out in batchwise mode or continuously.

- 30 In the process according to the invention, it is possible to work without an excess of nickel(II) halide or reducing agent, for example zinc, so that there is no need to remove them after the nickel(0) complex formation.

- 35 In a particular embodiment of the present invention, the process according to the invention comprises the following process steps:

- (1) drying an aqueous nickel(II) halide by azeotropic distillation,
- 40 (2) precomplexing the azeotropically dried nickel(II) halide in a solvent in the presence of a phosphorus ligand,

- (3) adding at least one reducing agent to the solution or suspension stemming from process step (2) at an addition temperature of from 20 to 120°C,
- (4) stirring the suspension or solution stemming from process step (3) for at a reaction temperature of from 20 to 120°C.

The precomplexation temperatures, addition temperatures and reaction temperatures may each independently be from 20°C to 120°C. Particular preference is given in the precomplexation, addition and reaction to temperatures of from 30°C to 80°C.

The precomplexation times, addition times and reaction times may each independently be from 1 minute to 24 hours. The precomplexation time is in particular from 1 minute to 3 hours. The addition time is preferably from 1 minute to 30 minutes. The reaction time is preferably from 20 minutes to 5 hours.

*Process step  $h_2^*$ ):*

A further preferred embodiment of process step  $h^*$ ), described here as process step  $h_2^*$ ), comprises the replenishment of the nickel(0) content of the streams 14 or 16, for example, by stirring in nickel powder. When this is done, free phosphorus ligand in the streams 14 or 16 is used as a complex formation partner or fresh ligand is added.

The catalyst compounds may be prepared from nickel powder with a suitable halide source as an initiator, for example a halide or an alkyl-substituted halide of phosphorus, arsenic or antimony, such as  $\text{CH}_3\text{PCl}_2$ ,  $\text{CH}_3\text{AsCl}_2$  or  $\text{CH}_3\text{SbCl}_2$ , or a suitable metal halide, elemental halogen such as chlorine, bromine or iodine, or the corresponding hydrogen halides or thionyl halide. Metal halides to be used in accordance with the invention are the halides of Cr, Ni, Ti, Cu, Co, Fe, Hg, Sn, Li, K, Ca, Ba, Sc, Ce, V, Mn, Be, Ru, Rh, Pd, Zn, Cd, Al, Th, Zr and Hf. The halide may be chloride, bromide or iodide. Particularly suitable halide sources are  $\text{PX}_3$ ,  $\text{TiX}_4$ ,  $\text{ZrX}_4$ ,  $\text{HfX}_4$  or  $\text{HX}$ , where X is chloride, bromide or iodide. When the inventive reaction is carried out, mixtures of 2 or more initiators or catalysts may also be used.

The catalyst regeneration may be carried out batchwise, for example in batch mode analogously to US 3,903,120, or continuously analogously to US 4,416,825, at temperatures of from 0 to 200°C, preferably from 25 to 145°C, more preferably from 50 to 100°C. The residence time of the catalyst may be varied within wide limits and is generally between 15 minutes and 10 h, preferably 20 minutes and 5 h, more preferably 30 minutes and 2 h.

When process step  $h_2^*$ ) is carried out instead of process step  $h_1^*$ ), the process steps  $i^*$ ),  $j^*$ ) and  $k^*$ ) may if appropriate be dispensed with fully or partly.

*Process step i\*):*

- If necessary, stream 18 may be concentrated before step i) by distillation, for example at pressures of from 0.1 to 5000 mbar (abs.), preferably from 0.5 to 1000 mbar (abs.) and in particular from 1 to 200 mbar (abs.), and temperatures of from 10 to 150°C, preferably from 40 to 100°C – or other suitable measures – for example to from 50 to 95%, preferably from 60 to 90%, of its original volume. In a particularly preferred embodiment, this stream contains after the concentration up to 10% by weight, i.e. from 0 to 10% by weight, preferably from 0.01 to 8% by weight, of pentenenitriles.

Step i\*): addition of the nonpolar aprotic liquid L

- In step i\*), a nonpolar aprotic liquid L is added to the stream 18 to obtain a stream 19. In this context, liquid means that the compound L is present in liquid form under the pressure and temperature conditions in step i\*); under other pressure and temperature conditions, L may also be solid or gaseous.

- Suitable nonpolar (or apolar) aprotic liquids L are all compounds liquid under the conditions of step i\*) which chemically or physically alter the catalyst, for example the Ni(0) complex with phosphorus ligands and/or the free phosphorus ligands, only insignificantly, if at all. Compounds suitable as the liquid L do not contain any ionizable proton in the molecule and generally have low relative dielectric constants ( $\epsilon_r < 15$ ) and low electrical dipole moments ( $\mu < 2.5$  Debye).

- Especially suitable are hydrocarbons which may, for example, be unhalogenated or halogenated, and also amines, especially tertiary amines, and carbon disulfide.

- In a preferred embodiment, the liquid L is a hydrocarbon H\*. Suitable hydrocarbons H\* are aliphatic, cycloaliphatic or aromatic. Suitable aliphatic hydrocarbons are, for example, linear or branched alkanes or alkenes having from 5 to 30, preferably from 5 to 16 carbon atoms, in particular pentane, hexane, heptane, octane, nonane, decane, undecane and dodecane (in each case all isomers).

- Suitable cycloaliphatic hydrocarbons have, for example, from 5 to 10 carbon atoms, such as cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclononane and cyclodecane. Substituted, in particular C<sub>1-10</sub>-alkyl-substituted, cycloaliphatics such as methylcyclohexane are also suitable. Suitable aromatic hydrocarbons are preferably those having from 6 to 20 carbon atoms, in particular benzene, toluene, o-, m- and p-xylene, naphthalene and anthracene. It is also possible to use substituted, preferably C<sub>1-10</sub>-alkyl-substituted aromatics such as ethylbenzene.

The hydrocarbon H\* is more preferably selected from the compounds mentioned below for the hydrocarbon H. Very particular preference is given to the hydrocarbon H\* being identical to the hydrocarbon H, i.e. the same hydrocarbon is used for the extraction in step j\*) and as the liquid L.

5

Configuration of the addition of the liquid

10 The nonpolar aprotic liquid L may be added to stream 18 in customary mixing apparatus. Because it is particularly simple from a process technology point of view, preference is given to mixing the nonpolar aprotic liquid L with stream 18 in step i\*) in a stirred vessel or a pumped circulation system.

15 Preference is given to intimately mixing the nonpolar aprotic liquid with stream 18. Suitable stirred vessels are customary liquid mixers which may be provided with intensively mixing mixer elements and/or static or mobile internals.

20 Preference is likewise given to the use of a pumped circulation system. It is typically operated in such a way that the ratio of amount in pumped circulation to output from the pumped circulation system is from 0.1 : 1 to 1000 : 1, preferably from 1 : 1 to 100 : 1 and more preferably from 2 : 1 to 25 : 1. Suitable circulation pumps are, for example, gear pumps or other customary pumps. The circulation pump preferably works against an overflow valve which opens at a defined pressure of, for example, from 3 to 10 bar (abs.).

25 When the same hydrocarbon is used in step i\*) and j\*), it is possible in both steps to use fresh hydrocarbon in each case. It is equally possible to reuse the hydrocarbon used in step i\*) in step j\*), or recycle the hydrocarbon used in step j\*) after step i\*) and reuse it there.

30 In a very particularly preferred embodiment, the liquid L is a substream of stream 22 (hydrocarbon H enriched with catalyst, see below) which is obtained in step j\*). This means that a portion of stream 22 is branched off in step j\*) and the branched-off portion is added to stream 18 in step i\*). In this embodiment, a portion of stream 22 is accordingly circulated.

35

In another, likewise preferred embodiment, the nonpolar aprotic liquid L is metered directly into a delay zone (see below), for example at the start thereof.

40 The liquid L is added generally at temperatures of from 0 to 150°C, preferably from 10 to 100°C and in particular from 20 to 80°C, and pressures of from 0.01 to 100 bar (abs.), preferably from 0.1 to 10 bar (abs.) and in particular from 0.5 to 5 bar (abs.).

The amount of liquid L required may vary within wide limits. It is generally lower than the amount of hydrocarbon H used with which extraction is effected in step j\*), but may also be greater. The amount of liquid L is preferably from 0.1 to 200% by volume, in particular from 1 to 50% by volume and more preferably from 5 to 30% by volume, based on the amount of the hydrocarbon H used for extraction in step j\*).

#### Optional treatment with ammonia or amine

When step h\*) comprises a redox regeneration, it is possible if appropriate to add ammonia or a primary, secondary or tertiary, aromatic or aliphatic amine to stream 18 or stream 19, or during step i\*) or during step j\*) itself. Aromatic includes alkylaromatic, and aliphatic includes cycloaliphatic.

It has been found that this ammonia or amine treatment can reduce the content of catalyst, in particular of nickel(0) complex or ligand in the extraction (step j\*)) in the second phase enriched with dinitriles (stream 23), i.e. in the extraction, the distribution of the Ni(0) complex or the ligands between the two phases is shifted in favor of the first phase (stream 22). The ammonia or amine treatment improves the catalyst enrichment in stream 22; this means smaller catalyst losses in the catalyst circuit and improves the economic viability of the hydrocyanation.

Accordingly, in this embodiment, the extraction is preceded by a treatment of stream 18 or of stream 19 with ammonia or an amine, or it is effected during the extraction. Treatment during the extraction is less preferred.

Particular preference is given to adding the ammonia or the amine together with the nonpolar aprotic liquid L. In particular, the liquid L and the ammonia or amine are added in the same mixing apparatus.

The amines used are monoamines, diamines, triamines or more highly functional amines (polyamines). The monoamines typically have alkyl radicals, aryl radicals or arylalkyl radicals having from 1 to 30 carbon atoms; suitable monoamines are, for example, primary amines, e.g. monoalkylamines, secondary or tertiary amines, e.g. dialkylamines. Suitable primary monoamines are, for example, butylamine, cyclohexylamine, 2-methylcyclohexylamine, 3-methylcyclohexylamine, 4-methylcyclohexylamine, benzylamine, tetrahydrofurfurylamine and furfurylamine. Useful secondary monoamines are, for example, diethylamine, dibutylamine, di-n-propylamine and N-methylbenzylamine. Suitable tertiary amines are, for example, trialkylamines having C<sub>1-10</sub>-alkyl radicals, such as trimethylamine, triethylamine or tributylamine.

Suitable diamines are, for example, those of the formula  $R^1-NH-R^2-NH-R^3$ , where  $R^1$ ,  $R^2$  and  $R^3$  are each independently hydrogen or an alkyl radical, aryl radical or arylalkyl radical having from 1 to 20 carbon atoms. The alkyl radical may be linear or, especially for  $R^2$ , also be cyclic. Suitable diamines are, for example, ethylenediamine, the  
5 propylenediamines (1,2-diaminopropane and 1,3-diaminopropane), N-methyl-ethylenediamine, piperazine, tetramethylenediamine (1,4-diaminobutane), N,N'-dimethylethylenediamine, N-ethylethylenediamine, 1,5-diaminopentane, 1,3-diamino-2,2-diethylpropane, 1,3-bis(methylamino)propane, hexamethylenediamine (1,6-diaminohexane), 1,5-diamino-2-methylpentane, 3-(propylamino)propylamine, N,N'-bis-  
10 (3-aminopropyl)piperazine, N,N'-bis(3-aminopropyl)piperazine and isophoronediamine (IPDA).

Suitable triamines, tetramines or more highly functional amines are, for example, tris(2-aminoethyl)amine, tris(2-aminopropyl)amine, diethylenetriamine (DETA),  
15 triethylenetetramine (TETA), tetraethylenepentamine (TEPA), isopropylenetriamine, dipropylenetriamine and N,N'-bis(3-aminopropylethylenediamine). Aminobenzylamines and aminohydrazides having 2 or more amino groups are likewise suitable.

Of course, it is also possible to use mixtures of ammonia with one or more amines, or  
20 mixtures of a plurality of amines.

Preference is given to using ammonia or aliphatic amines, in particular trialkylamines having from 1 to 10 carbon atoms in the alkyl radical, e.g. trimethylamine, triethylamine or tributylamine, and also diamines such as ethylenediamine, hexamethylenediamine  
25 or 1,5-diamino-2-methylpentane.

Particular preference is given to ammonia alone, i.e. particular preference is given to using no amine in addition to ammonia. Anhydrous ammonia is very particularly preferred; in this context, anhydrous means a water content below 1% by weight,  
30 preferably below 1000 ppm by weight and in particular below 100 ppm by weight.

The molar ratio of amine to ammonia may be varied within wide limits, and is generally from 10 000 : 1 to 1 : 10 000.

35 Factors determining the amount of ammonia or amine used include the type and amount of catalyst, for example of the nickel(0) catalyst, and/or of the ligands, and, where used, the type and amount of Lewis acid which is used as a promoter in the hydrocyanation. Typically, the molar ratio of ammonia or amine to Lewis acid is at least 1 : 1. The upper limit of this molar ratio is generally uncritical and is, for example,  
40 100 : 1, but the excess of ammonia or amine should not be so great that the Ni(0) complex or ligands thereof decompose. The molar ratio of ammonia or amine to Lewis acid is preferably from 1 : 1 to 10 : 1, more preferably from 1.5 : 1 to 5 : 1, and in

particular about 2 : 1. Where a mixture of ammonia and amine is used, these molar ratios apply to the sum of ammonia and amine.

- 5 The temperature in the treatment with ammonia or amine is typically not critical and is, for example, from 10 to 140°C, preferably from 20 to 100°C and in particular from 20 to 90°C. The pressure is generally also not critical.

- 10 The ammonia or the amine may be added to stream 18 in gaseous, liquid (under pressure) or dissolved form in a solvent. Suitable solvents are, for example, nitriles, especially those which are present in the hydrocyanation, and also aliphatic, cycloaliphatic or aromatic hydrocarbons, as are used as extractants in the process according to the invention, for example cyclohexane, methylcyclohexane, n-heptane or n-octane.

- 15 The ammonia or amine is added in customary apparatus, for example those for gas introduction or in liquid mixers. The solid which precipitates in many cases may either remain in stream 18, i.e. a suspension is fed to the extraction, or be removed as described below.

- 20 Optional removal of solids

In a preferred embodiment, solids which precipitate out in step i\*) of the process are removed from stream 19 before the extraction (step j\*)).

- 25 In many cases, this allows the extraction performance of the process according to the invention to be improved further, since solids which occur often reduce the separating performance of the extraction apparatus. It has also been found that a solids removal before the extraction in many cases once again distinctly reduces or fully suppresses the undesired formation of rag.

- 30 Preference is given to configuring the solids removal in such a way that solid particles having a hydraulic diameter greater than 5 µm, in particular greater than 1 µm and more preferably greater than 100 nm are removed.

- 35 For the solids removal, customary processes may be used, for example filtration, crossflow filtration, centrifugation, sedimentation, classification or preferably decanting, for which common apparatus such as filters, centrifuges or decanters may be used.

- 40 Temperature and pressure in the solids removal are typically not critical. For example, it is possible to work in the temperature and pressure ranges mentioned above or below.

The solids removal may be carried out before, during or after the optional treatment of stream 18 or of stream 19 with ammonia or amine. Preference is given to removal during or after the ammonia or amine treatment, and particular preference to removal after it.

5

When the solids are removed during or after the ammonia or amine treatment, the solids are usually compounds of ammonia or amine with the Lewis acid used or the promoter which are sparingly soluble in stream 18. When, for example,  $\text{ZnCl}_2$  is used, substantially sparingly soluble  $\text{ZnCl}_2 \cdot 2 \text{NH}_3$  precipitates out in the ammonia treatment.

10

When the solids are removed before the ammonia or amine treatment, or if there is no treatment at all with ammonia or amine, the solids are generally nickel compounds in the +II oxidation state, for example nickel(II) cyanide or similar cyanide-containing nickel(II) compounds, or are Lewis acids or compounds thereof. The compounds mentioned may precipitate out, for example, because their solubility has been reduced, for example, by temperature change.

15

#### Optional delay zone

20

Stream 19 as the effluent from step i\*) may be transferred directly into step j\*), for example through a pipeline. Directly means that the average residence time of stream 19 in the pipeline is less than 1 min.

25

However, in a preferred embodiment of the process according to the invention, stream 19 is conducted through a delay zone after step i\*) and before step j\*). The delay zone is consequently downstream of the addition of the liquid L and upstream of the extraction.

30

Suitable delay zones are, for example, pipelines, static mixers, stirred or unstirred vessels or vessel batteries, and combinations of these elements. The delay zone is preferably configured in such a way that the average residence time of stream 19 in the delay zone is at least 1 min, preferably at least 5 min.

35

The optional solids removal described above may also be effected in the delay zone. In this case, the delay zone serves as a calming zone in which the solids can settle. In this way, the delay zone functions like a decanter or crossflow filter. It may be provided with apparatus for conveying and/or for the discharge of solids.

40

As mentioned, in a preferred embodiment, the nonpolar aprotic liquid L is metered directly into the delay zone, for example at the start thereof. In this embodiment, particular preference is given to selecting a delay zone which ensures intimate mixing

of stream 18 and liquid L. As likewise already described, the delay zone may bring about a phase separation of stream 19.

5 The delay zone is generally operated at temperatures of from 0 to 200°C, preferably from 10 to 150°C and in particular from 20 to 100°C, and pressures of from 0.01 to 100 bar (abs.), preferably from 0.1 to 10 bar (abs.) and in particular from 0.5 to 5 bar (abs.).

10 In a preferred embodiment of the invention, the flow rate of stream 19 in all of the pipelines used in the process according to the invention is at least 0.5 m/s, in particular at least 1 m/s and more preferably at least 2 m/s.

15 The stream 19 obtained in step a) is, if appropriate after the treatment with ammonia or amines, and/or after the solids removal and/or after passing through the delay zone, extracted in step j\*).

*Process step j\*):*

20 Process principle

25 The process according to the invention is suitable for the extractive purification of Ni(0) complexes which contain phosphorus ligands and/or free phosphorus ligands in stream 19 or, if appropriate, stream 18 when step i\*) is not performed, by adding a C6-dinitrile such as adiponitrile (ADN), 2-methylglutaronitrile (MGN) or 2-ethylsuccinonitrile (ESN) with regard to the disruptive component(s) which induce increased formation of C5 mononitriles not amenable to hydrocyanation, such as E-2-methyl-2-butenenitrile and/or Z-2-methyl-2-butenenitrile.

30 In addition, the catalyst losses are reduced in the extraction by introducing a hydrocarbon H in stream 21 at an inlet point which is closer to the outlet point of the extract than to the inlet point of feed stream 18 or 19. The inlet point of the dinitrile (stream 20) is closer to the outlet point of the raffinate than the inlet point of feed stream 18 or 19. In this context, closer should be understood in the sense of the  
35 number of theoretical plates between two points. Between the inlet points of streams 18 or 19 and 21 there are generally from 0 to 10, preferably from 1 to 7, theoretical extraction (separation) stages (re-extraction zone for the catalyst); between the inlet points of streams 18 or 19 and 20 there are generally from 1 to 10, preferably from 1 to 5, theoretical extraction (separation) stages (purification zone with regard to disruptive  
40 component(s)).

In general, a first phase [raffinate; stream 22] is formed at a temperature T (in °C) and is enriched in the Ni(0) complexes or ligands mentioned compared to stream 18, and a second phase [extract; stream 23; enriched disruptive component(s)], which is enriched in dinitriles compared to stream 18. Usually, the first phase is the lighter phase, i.e. the upper phase, and the second phase the heavier phase, i.e. the lower phase.

After the phase separation, the upper phase contains preferably between 50 and 99% by weight, more preferably between 60 and 97% by weight, in particular between 80 and 95% by weight, of the hydrocarbon used for the extraction.

10

The Lewis acid which is in some cases (specifically when the redox catalyst regeneration is implemented in process step h<sub>1</sub>\*) present in the inlet stream of the extraction remains preferably for the most part and more preferably fully in the lower phase. Here, fully means that the residual concentration of the Lewis acid in the upper phase is preferably less than 1% by weight, more preferably less than 0.5% by weight, in particular less than 500 ppm by weight.

15

The discharge of the disruptive component(s) improves the process selectivity, since fewer C5 mononitriles not amenable to hydrocyanation are formed (reduction of incorrect isomerizations).

20

A particular advantage of embodiment III is that dinitriles such as ADN, MGN, ESN, which form in small amounts in process step e\*) and thus accumulate in stream 10, are discharged at least partly with the lower phase of the extraction.

25

A further particular advantage of the employment of process step j\*) is that the reactant used in process step e\*) may be stabilizer-containing butadiene. Such a stabilizer may be, for example, tert-butylpyrocatechol. This stabilizer is discharged via the lower phase of the extraction. Thus, no catalyst-damaging concentrations of the stabilizer can be accumulated in the catalyst circuit.

30

A further particular advantage is that a redox regeneration of the catalyst for the replenishment of the Ni(0) value according to h<sub>1</sub>\*) can be undertaken in process step h\*), since the Lewis acid formed in this way is discharged via the lower phase of the extraction. This Lewis acid would otherwise lead to increased dinitrile formation in the first hydrocyanation (process step e\*)).

35

The lower phase of the extraction may suitably be worked up, so that the dinitriles present therein may be used again as a feed to the extraction. Such a workup may be effected, for example, by distillation (DE-A-10 2004 004683; stream 7 from step c)).

40

### Configuration of the extraction

- The extractive tasks may preferably be achieved by using a countercurrent extraction column having a re-extraction zone. However, identically functioning combinations of any suitable apparatus known to those skilled in the art, such as countercurrent extraction columns, mixer-settler units or combinations of mixer-settler units with columns, for example a series connection of two countercurrent extraction columns (for example one for the purification with regard to disruptive component(s), the other for the re-extraction of the catalyst) are also. Particular preference is given to the use of countercurrent extraction columns which are in particular equipped with sheet metal packings as dispersing elements. In a further particularly preferred embodiment, the extraction is performed in countercurrent in compartmented, stirred extraction columns.
- With regard to the direction of dispersion, in a preferred embodiment of the process, the hydrocarbon is used as the continuous phase and stream 18 of the hydrocyanation as the disperse phase. This generally shortens the phase separation time and reduces the formation of rag. However, the reverse direction of dispersion is also possible, i.e. stream 18 as the continuous and hydrocarbon as the disperse phase. The latter is especially true when the rag formation is reduced or fully suppressed by preceding solids removal (see below), higher temperature in the extraction or phase separation or use of a suitable hydrocarbon. Typically, the direction of dispersion more favorable for the separating performance of the extraction apparatus is selected.
- In the extraction, the following ratios of the feeds are set:  
Stream 20 to the sum of stream 18 or 19 and stream 21 in the range from 0.01 to 10 kg/kg, preferably from 0.05 to 5 kg/kg. Stream 21 to stream 20 in the range from 0.05 to 20 kg/kg, preferably from 1 to 10 kg/kg. Stream 21 to stream 18 or 19 in the range from 0.05 to 20 kg/kg, preferably from 0.5 to 8 kg/kg.
- The absolute pressure during the extraction is preferably from 10 kPa to 1 MPa, more preferably from 50 kPa to 0.5 MPa, in particular from 75 kPa to 0.25 MPa (absolute).
- The extraction is preferably carried out at a temperature from  $-15$  to  $120^{\circ}\text{C}$ , in particular from  $20$  to  $100^{\circ}\text{C}$  and more preferably from  $30$  to  $80^{\circ}\text{C}$ . It has been found that the rag formation is lower at higher temperature of the extraction.

### Configuration of the phase separation

- Depending upon the apparatus configuration, the phase separation may also be viewed in spatial and temporal terms as the last part of the extraction. For the phase separation, a wide pressure, concentration and temperature range may typically be

selected, and the optimal parameters for the particular composition of the reaction mixture may be determined readily by a few simple preliminary experiments.

5 The temperature T in the phase separation is typically at least 0°C, preferably at least 10°C, more preferably at least 20°C. Typically, it is at most 120°C, preferably at most 100°C, more preferably at most 95°C. For example, the phase separation is carried out at from 0 to 100°C, preferably from 60 to 95°C. It has been found that the rag formation is lower at higher temperature of the phase separation.

10 The pressure in the phase separation is generally at least 1 kPa, preferably at least 10 kPa, more preferably 20 kPa. In general, it is at most 2 MPa, preferably at most 1 MPa, more preferably at most 0.5 MPa.

15 The phase separation time, i.e. the time from the mixing of stream 18 with the hydrocarbon (extractant) to the formation of a uniform upper phase and a uniform lower phase, may vary within wide limits. The phase separation time is generally from 0.1 to 60 min, preferably from 1 to 30 min and in particular from 2 to 10 min. When the process according to the invention is carried out on the industrial scale, a phase separation time of not more than 15 min, in particular not more than 10 min, is typically  
20 technically and economically viable.

It has been found that the phase separation time is reduced in an advantageous manner especially when long-chain aliphatic alkanes such as n-heptane or n-octane are used as the hydrocarbon H.

25 The phase separation may be carried out in one or more apparatuses known to those skilled in the art for such phase separations. In an advantageous embodiment, the phase separation may be carried out in the extraction apparatus, for example in one or more mixer-settler combinations, or by equipping an extraction column with a calming  
30 zone.

In the phase separation, two liquid phases are obtained, of which one phase has a higher proportion of the nickel(0) complex with phosphorus ligands and/or free phosphorus ligands, based on the total weight of this phase, than the other phase or  
35 other phases. The other phase is enriched in the disruptive component(s).

#### Dinitrile

40 Stream 20 which is conducted to the extraction as a feed stream comprises predominantly dinitriles, preferably C6 dinitriles, especially preferably adiponitrile (ADN), 2-methylglutaronitrile (MGN), 2-ethylsuccinonitrile (ESN) or mixtures thereof. The content in this stream of dinitriles is preferably greater than 50% by weight, more

preferably greater than 70% by weight, especially preferably greater than 90% by weight. Processes for preparing dinitriles, in particular C6 dinitriles, are known per se. One possible such process is described in DE-A-10 2004 004683. Streams of C6 dinitriles prepared in this way, in particular streams 15, 16 and 17 from process step h) of DE-A-10 2004 004683, are generally suitable to be used here as stream 20.

Dinitriles are added preferably to the extent that a phase separation is effected in the extraction stage k\*).

#### 10 Hydrocarbon

The hydrocarbon is the extractant. It preferably has a boiling point of at least 30°C, more preferably at least 60°C, in particular at least 90°C, and preferably at most 140°C, more preferably at most 135°C, in particular at most 130°C, in each case at a pressure of 10<sup>5</sup> Pa absolute.

A hydrocarbon, this referring in the context of the present invention to an individual hydrocarbon or to a mixture of such hydrocarbons, may more preferably be used for the removal, especially by extraction, of adiponitrile from a mixture comprising adiponitrile and the Ni(0)-containing catalyst, said hydrocarbon having a boiling point in the range between 90°C and 140°C. From the mixture obtained by this process after the removal, the adiponitrile may be obtained advantageously by distillative removal of the hydrocarbon, the use of a hydrocarbon having a boiling point in the range mentioned permitting a particularly economically viable and technically simple removal by virtue of the possibility of condensing the hydrocarbon distilled off with river water.

Suitable hydrocarbons are described, for example, in US 3,773,809, column 3, line 50-62. Useful hydrocarbons are preferably selected from cyclohexane, methylcyclohexane, cycloheptane, n-hexane, n-heptane, isomeric heptanes, n-octane, isooctane, isomeric octanes such as 2,2,4-trimethylpentane, cis- and trans-decalin or mixtures thereof, in particular of cyclohexane, methylcyclohexane, n-heptane, isomeric heptanes, n-octane, isomeric octanes such as 2,2,4-trimethylpentane, or mixtures thereof. Particular preference is given to using cyclohexane, methylcyclohexane, n-heptane or n-octane.

Very particular preference is given to n-heptane or n-octane. In the case of these hydrocarbons, the undesired rag formation is particularly low. Rag refers to a region of incomplete phase separation between upper and lower phase, usually a liquid/liquid mixture, in which solids may also be dispersed. Excessive rag formation is undesired, since it hinders the extraction and the extraction apparatus can under some circumstances be flooded by rag, as a result of which it can no longer fulfill its separating task.

- The hydrocarbon used is preferably anhydrous, anhydrous meaning a water content of below 100 ppm by weight, preferably below 50 ppm by weight, in particular below 10 ppm by weight. The hydrocarbon may be dried by suitable processes known to those skilled in the art, for example by adsorption or azeotropic distillation. The drying may be effected in a step preceding the process according to the invention.

*Process step k\*):*

- 10 In **process step (k\*)**, a distillation of stream 22 to obtain a stream 25 comprising the at least one catalyst and a stream 24 comprising the extractant takes place.

This process step serves substantially to recover the catalyst and the extractant.

- 15 Process step (k\*) may be carried out in any suitable apparatus known to those skilled in the art. The distillation of process step k\*) takes place preferably in one or more evaporation stages, or else rectification columns/distillation columns.

- 20 The internals used for the rectification columns/distillation columns are preferably structured sheet metal packing, structured fabric packing, bubble-cap trays, dual-flow trays or beds of random packings or combinations of two or more of these classes of separating internals. The rectification column/distillation column of process step k\*) may be configured with one or more liquid or gaseous side draws. The rectification column/distillation column from process step k\*) may be configured as a dividing wall column having one or more gaseous or liquid side draws present.

- 25 The one or more evaporator stages or the rectification column/distillation column of process step k\*) may in particular be equipped with falling-film evaporators, thin-film evaporators, natural-circulation evaporators, forced-circulation flash evaporators and multiphase helical-tube evaporators.

- 30 In a further embodiment of the process according to the invention, at least one of the evaporator units of process step k\*) is operated with a divided column bottom, in which case the circulation stream, generally large in relation to the bottom draw stream, is conducted from a first column bottom of the evaporator stage in question to the evaporator, but the liquid output stream from the evaporator is not returned directly into the column bottom, but rather collected in a second column bottom which is separate from the first column bottom, the bottom draw stream is obtained from the second column bottom and the remaining excess from the evaporator circulation stream is allowed to overflow into the first column bottom to obtain, as the bottom draw stream from the second column bottom, a mixture which is depleted in low boilers compared to the draw from the first column bottom.

The absolute pressure in process step k\*) is preferably from 0.001 to 2 bar(a), more preferably from 0.01 to 0.5 bar(a), in particular from 0.09 to 0.12 bar(a). The distillation is carried out in such a way that the temperature in the bottom of the distillation apparatus is preferably from 40 to 150°C, more preferably from 70 to 120°C, in particular from 80 to 100°C. The distillation is carried out in such a way that the temperature at the top of the distillation apparatus is preferably from -15 to 100°C, more preferably from 0 to 60°C, in particular from 20 to 50°C. In a particularly preferred embodiment of the process according to the invention, the aforementioned temperature ranges are maintained both at the top and in the bottom.

In the removal of the extractant to recover the catalyst in process step k\*), 3-pentenitrile may be added if appropriate to the distillation as an intermediate boiler. This solvent change in some cases has the advantage that an effective depletion of the extractant from the high-boiling catalyst stream becomes possible at evaporator temperatures which are low enough not to thermally damage the nickel catalyst used in each case, especially when chelate ligands are used, and to thermally conserve it when monodentate ligands are used, the pressure still being high enough in order still to be able to condense the extractant, comparatively low-boiling in comparison to the catalyst constituents, at the top of the evaporator stage or distillation column at customary cooling water temperatures of from 25 to 50°C. The solvent change additionally in some cases has the advantage that the flowability and the monophasicity of the catalyst solution is ensured, since, depending on the temperature and residual content of extractants – without the addition of 3-pentenitrile – catalyst constituents can in some cases crystallize out. In this case, 3-pentenitrile which, for example, depending on the pressure conditions, can be removed from the cyclohexane or methylcyclohexane or heptane or n-heptane extractants only with difficulty or cannot be removed completely at all owing to minimum vapor pressure azeotrope formation does not have a disruptive effect on the process according to the invention at a content of preferably up to 10% by weight, more preferably up to 5% by weight, in particular up to 1% by weight, based on the total amount of the extractant inlet stream to the extraction column in process step j\*).

In a preferred embodiment of the process according to the invention, the stream 24 obtained in process step k\*), comprising the extractant, is recycled at least partly into the extraction step j\*). The recycled stream 24 is dried if appropriate before the extraction step j\*), so that the water content in this stream is preferably less than 100 ppm by weight, more preferably less than 50 ppm by weight, in particular less than 10 ppm by weight.

In a further preferred embodiment of the process according to the invention, the stream 25 obtained in process step k\*), comprising the catalyst, is recycled at least partly into

the hydrocyanation of process step e\*) or into the isomerization of process step a\*). In a preferred embodiment of the process according to the invention, the proportion of extractant in stream 25 is preferably less than 10% by weight, more preferably less than 5% by weight, in particular less than 1% by weight, based on the total amount of stream 25.

Preferred embodiments of the catalyst flow control through process stages a\*) to k\*) are described hereinbelow with reference to schemes 1 to 5. Process step i\*) is not present in schemes 1 to 5, but can in each case be carried out between h\*) and j\*). In schemes 1 to 5, process step h\*) is described by way of example in the embodiment as process step h<sub>1</sub>\*). Alternatively, the embodiment may also be carried out as process step h<sub>2</sub>\*). In these cases, the nickel(II) chlorides would be replaced by nickel powder, and there is no reducing agent (red.), nor is there any Lewis acid (LA). ADN synonymously represents dinitrile streams; heptane synonymously represents hydrocarbons as the extractant. Cat. in each case means catalyst complexes plus free ligand. The dashed lines in schemes 1 to 5 denote optional bypass substreams of the catalyst streams.

A particular embodiment of the process with regard to the catalyst flow control is shown in scheme 1. In this scheme, the catalyst-conducting stages are combined in a single catalyst circuit. The sequence of the process stages starting from the first hydrocyanation is e\*), f\*), a\*), b\*), c\*), h\*), if appropriate i\*), j\*), k\*), before being fed back to e\*). If appropriate, a substream of the catalyst may be recycled past stages h\*), i\*), j\*) and k\*), and directly into e\*). Process stage a\*) is fed here with unseparated mixture of 2-methyl-3-butenenitrile and 3-pentenitrile, i.e. d\*) or g\*) is performed after a\*).

A further particular embodiment of the process with regard to the catalyst flow control is shown in scheme 2. In this scheme, the catalyst-conducting stages are combined in a single catalyst circuit. Starting from the first hydrocyanation, the sequence of the process stages is e\*), f\*), a\*), b\*), c\*), h\*), if appropriate i\*), j\*), k\*), before being fed back to e\*). If appropriate, a substream of the catalyst may be recycled past stages h\*), i\*), j\*) and k\*), and directly into e\*). Process stage a\*) is fed here with 2-methyl-3-butenenitrile depleted in 3-pentenitrile, i.e. d\*) or g\*) is performed before a\*).

A further particular embodiment of the process with regard to the catalyst flow control is shown in scheme 3. In this scheme, a catalyst stream is circulated through stages e\*) and f\*). From this stream, a substream is discharged and used as catalyst feed for stage a\*). Subsequently, this stream is fully, if appropriate partly, fed through stages b\*), c\*), h\*), if appropriate i\*), j\*) and k\*), back into e\*). The isomerization stage a\*) is fed with 2-methyl-3-butenenitrile depleted in 3-pentenitrile, i.e. d\*) or g\*) is performed before a\*). Equally, d\* or g\* may also be performed after a\*.

A further particular embodiment of the process with regard to the catalyst flow control is shown in scheme 4. In this scheme, two catalyst circuits are formed. Catalyst circuit 1 comprises the stages e\*) and f\*), catalyst circuit 2 the stages a\*), b\*), c\*). From both streams, substreams, if appropriate also the particular overall catalyst streams, are conducted via stages h\*), if appropriate i\*), j\*) and k\*), in order to purify the catalyst of disruptive component(s) and/or to replenish the Ni(0) content. The proportion from catalyst circuit 2 conducted through the extraction is preferably greater than that from catalyst circuit 1. If appropriate, the entire stream from catalyst circuit 2 is conducted through the extraction. The two catalyst circuits are coupled to one another only via stages h\*), if appropriate i\*), j\*) and k\*). The division of the stream from k\*) for feeding of a\*) or e\*) corresponds generally to the ratio of the feed streams to h\*) from a\*) and e\*). The isomerization stage a\*) is fed with 2-methyl-3-butenenitrile depleted in 3-pentenitrile, i.e. d\*) or g\*) is performed before a\*). Equally, d\* or g\* may also be performed after a\*.

A further particular embodiment of the process with regard to the catalyst flow control is shown in scheme 5. According to this, a catalyst circuit is operated via stages a\*), b\*), c\*), h\*), if appropriate i\*), j\*) and k\*). From this catalyst circuit, a substream is drawn off before h\*) and the first hydrocyanation e\*) is operated with it. The stream is recycled to h\*) via f\*). If appropriate, the recycling may also be directly to a\*). A substream of the isomerization catalyst circuit may also be recycled from c\*) directly into a\*). The isomerization stage a\*) is fed with 2-methyl-3-butenenitrile depleted in 3-pentenitrile, i.e. d\*) or g\*) is performed before a\*). Equally, d\* or g\* may also be performed after a\*.

The present invention is illustrated in detail with reference to the examples detailed hereinbelow.

30

### Working examples

In the examples, the following abbreviations are used:

35	hydrogen cyanide:	hydrogen cyanide
	T3PN:	trans-3-pentenitrile
	C3PN:	cis-3-pentenitrile
	4PN:	4-pentenitrile
	E2M2BN:	(E)-2-methyl-2-butenenitrile
40	T2PN:	trans-2-pentenitrile
	C2PN:	cis-2-pentenitrile
	ADN:	adiponitrile

MGN:	methylglutaronitrile
VAN :	valeronitrile
VCH :	4-vinylcyclohexene
BD:	1,3-butadiene
5 TBP:	tert-butylpyrocatechol
C2BU:	cis-2-butene
LA:	Lewis acid

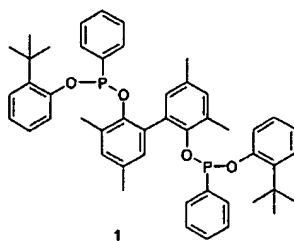
10 In the examples, the process steps are reported in a chronological sequence and thus deviate from the designation in the description and in the claims. Data in % or ppm which is not characterized in detail are % by weight and ppm by weight respectively.

### Example 1:

15

Example 1 is illustrated with reference to Figure 3.

In Example 1, a catalyst system based on nickel(0) complexes with a mixture of ligands is used for the hydrocyanation of butadiene. The ligand mixture for the hydrocyanation  
20 contains approx. 60 mol% of tri(m/p-tolyl) phosphite and 40 mol% of the chelate phosphonite 1:



25 In a step (1), the following streams are conducted into a loop reactor R1 of capacity 25 l which is equipped with a nozzle, impulse exchange tube, external pumped circulation system and in a heat exchanger disposed in the pumped circulation system for removing the energy of reaction and is heated to 357 K:

- 30 (1) 10 kg/h of liquid unstabilized hydrogen cyanide freed of water by distillation,
- (2) 22 kg/h of commercial BD containing 0.25% C2BU which has been treated by contact with alumina in order to remove water and TBP stabilizer,
- 35 (3) 8 kg/h of recycled BD from K2a in step (2) (stream 9), so that the entire BD feed to the reactor R1 which is obtained is a stream of 30 kg/h containing 90% BD, 5% C2BU and 5% 1-butene,

(4) 21 kg/h of nickel(0) catalyst solution, obtained as described below in this example, as stream 10a from column K2b.

5 The stream 8 withdrawn from the reactor R1 (63 kg/h) contains a total of 11% BD and C2BU, corresponding to a conversion of 79% BD, and also a total of 63% pentenenitriles, 31% T3PN, 29% 2M3BN and small amounts of Z2M2BN and E2M2BN, and further pentenenitrile isomers (T2PN, C2PN, C3PN, 4PN), and also the catalyst constituents and catalyst degradation products and MGN.

10

Stream 8 is fed in a step (2) to a distillation column K2a which is operated with rectifying section and stripping section and is equipped with a falling-film evaporator and separated bottom, and also column internals having structured packing which generate 10 theoretical plates. Column K2a is operated at the top with a direct  
15 condenser which consists of a column section equipped with structured packing and having a total collecting cup, pumped circulation system and external heat exchanger. The column K2a is operated at an absolute top pressure of 2.0 bar, top temperature 288 K and bottom draw temperature 363 K.

20 Via the top of column K2a is obtained stream 9 which, as described at the outset, is metered into the reactor R1 as a recycle stream. The reflux ratio at the top of the column K2a is adjusted in such a way that stream 9 contains approx. 100 ppm of 2M3BN.

25 Via the bottom of the column K2a are obtained 59 kg/h of a stream 1b which contains 2.9% BD, 4.6% C2BU, 67% pentenenitriles, and also additionally the catalyst constituents. In relation to BD, C2BU is distinctly enriched compared to the feed.

Within step (2), stream 1b is conducted into a distillation column K2b which is operated  
30 in stripping mode and is equipped with falling-film evaporator, top condenser with postcondenser and also column internals having structured packing which generate 10 theoretical plates. The column is operated at an absolute top pressure of 150 mbar, top temperature 329 K and bottom draw temperature 373 K. The vapor stream of the column is partly condensed at 308 K and treated with a postcondenser at 263 K. The  
35 BD stream 2c, thus depleted of 2M3BN and other pentenenitriles, is compressed in a compressor V2 to an absolute pressure of 1.2 bar. The compressed gas stream is to a great extent condensed at 279 K to obtain a stream 2e (5 kg/h), and a substream 2d (47 l (STP)/h, containing 44% C2BU) is disposed of in gaseous form. Stream 2e is recycled in liquid form into the condensate collecting vessel of the column K2a.

40

In a gaseous side draw of the column K2b, stream 11 is obtained (40 kg/h) and contains approx. 100 ppm of BD, 46% 2M3BN and 48% T3PN, and also, to a smaller

extent, E2M2BN and Z2M2BN in addition to other pentenenitrile isomers. The position of the side draw is selected in such a way that the component 2M3BN in the stream 10 obtained via the bottom is depleted in relation to T3PN in a stripping section below the side draw.

5

Into column K2b are conducted 13 kg/h of a catalyst stream which is obtained as described in Example 1 of the German patent application having the title "Preparation of dinitriles" to BASF AG (B03/0525) as the side draw of the column K4 from step (4), containing a total of 73% pentenenitriles, 0.5% Ni(0), 18% ligand mixture and approx.

10

5% ADN.

Via the bottom of the column K2b is obtained the catalyst stream 10 containing 0.5% Ni(0), approx. 100 ppm of 2M3BN and 73% remaining pentenenitriles. Stream 10 is split into substream 10a (21 kg/h) which is recycled into the reactor R1. The other portion (10b) (5.4 kg/h) is fed to a regeneration according to DE-A-103 51 002, in order, after regeneration, to be used, for example, in the hydrocyanation of 3-pentenenitrile as described in Example 1 of DE-A-102 004 004 683.

In a step (3), stream 11 is conducted to a distillation column K3 which is equipped with circulation evaporator and top condenser, and also with structured packing which generate 30 theoretical plates. The column K3 is operated at an absolute top pressure of 180 mbar, top temperature 345 K and bottom draw temperature 363 K.

Into the column K3 are conducted 39 kg/h of recycle stream 5 from column K5 in step (5), containing 54% T3PN, 23% 2M3BN and 16% Z2M2BN, and also, in small amounts, further pentenenitrile isomers.

Via the top of column K3 are obtained 40 kg/h of a stream 13 containing 10% T3PN, 68% 2M3BN, 16% Z2M2BN, and also a total of 0.1% BD and C2BU and small amounts of other pentenenitrile isomers (T2PN, C2PN, C3PN, 4PN).

Via the bottom of column K3 are obtained 39 kg/h of stream 12 containing 97% in total of T3PN, C3PN and 4PN, and small amounts of other pentenenitrile isomers (T2PN, C2PN), and also approx. 100 ppm of 2M3BN and approx. 1% E2M2BN.

35

In Example 1, a catalyst system based on nickel(0) complexes with a mixture of ligands is used for the isomerization of 2M3BN to T3PN. The ligand mixture for the isomerization (referred to hereinbelow as isomerization ligand) comprises mixed phosphite ligands of the P(OR)(OR')(OR'') class having randomly distributed R, R', R'' from the group of m-tolyl, p-tolyl, o-isopropylphenyl, and approx. 40 mol% of the sum of the R, R', R'' radicals are o-isopropylphenyl radicals. Such ligand mixtures are obtained in the reaction of a mixture of m- and p-cresol having a ratio of 2:1 of m-cresol

40

compared to p-cresol and a stoichiometrically matched amount of o-isopropylphenol with a phosphorus trihalide.

5 In a step (4), stream 13 is conducted, together with a catalyst recycle stream 3a and a catalyst supplementation stream, into a reactor R2, designed as a tubular reactor, which is heated to 393 K. As the sum of recycled catalyst and fresh catalyst, 56 kg/h of a mixture having 20% T3PN, 5% 2M3BN and other pentenenitrile isomers, 55% isomerization ligand and 0.5% nickel(0), and also a small content of catalyst degradation products, are conducted into reactor R2.

10

As the product from reactor R2, 96 kg/h of stream 1 are obtained, containing 34% T3PN, 12.3% 2M3BN and small amounts of other pentenenitrile isomers (T2PN, C2PN, C3PN, 4PN), corresponding to a conversion of 60% 2M3BN.

15 In a step (5), stream 1 is conducted into a distillation column K5 which is operated as a rectifying column and is equipped with a falling-film evaporator, top condenser, reflux divider, gaseous side draw in the bottom region of the column, and also column internals with structured packing which generate 30 theoretical plates. The column is operated at an absolute top pressure of 250 mbar, top temperature 353 K and bottom  
20 draw temperature 373 K.

In column K5, the recovered catalyst stream 3 (56 kg/h) is obtained via the bottom, containing 20% T3PN in addition to other pentenenitriles, approx. 5% MGN and also 0.5% Ni(0) and 54% isomerization ligand. A small portion of stream 3 is discharged as  
25 stream 3b to restrict the accumulation of catalyst deactivation components and MGN. To supplement the amount of catalyst discharged, sufficient fresh catalyst containing 15% T3PN in addition to other pentenenitrile isomers, 1% Ni(0) and 80% isomerization ligand is metered in so that the Ni(0) content in the catalyst feed to reactor R2 is kept at 0.5%.

30

In column K5, a stream 4 is obtained via the top (0.8 kg/h), containing a total of 0.5% BD and C2BU, 50% 2M3BN, 41% Z2M2BN, and also small amounts of vinylcyclohexene (VCH) which is firstly present in traces in the BD starting material and secondly formed in small amounts in the hydrocyanation of butadiene, and ultimately  
35 accumulates in the 2M3BN cycle of the isomerization and has to be discharged together with 2M3BN, since the vapor pressures of 2M3BN and VCH are so close to one another that a separation by conventional distillation is not possible. The reflux ratio of column K5 is adjusted in such a way that 10 ppm of T3PN are present in stream 4. The draw rate of stream 4 from the top of column K5 is adjusted in such a  
40 way that a total of 20% Z2M2BN and VCH are present in the top draw stream 13 of distillation column K3.

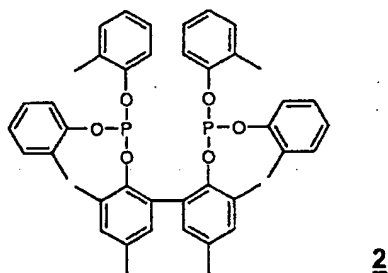
In column K5, a stream 5 is obtained via the gaseous side draw (39 kg/h) which, in addition to 3-pentenitriles, comprises substantially the 2M3BN unconverted in the isomerization and, after condensation, is recycled in liquid form into column K3 as described above.

5

**Example 2:**

Example 2 is illustrated with reference to Figure 4.

- 10 In Example 2, a catalyst system based on nickel(0) complexes with chelate phosphite 2 as a ligand is used for the hydrocyanation of BD:



- 15 In a step (1), the following streams are conducted into a system composed of two reactors, R1a and R1b, each of capacity 12 l, each of which is equipped with a nozzle, impulse exchange tube, external pumped circulation system and in a heat exchanger disposed in the pumped circulation system to remove the energy of reaction, and are heated to 363 K:
- 20 (1) 6 kg/h of liquid, unstabilized hydrogen cyanide freed of water by distillation to R1a,
- (2) 6 kg/h of liquid, unstabilized hydrogen cyanide freed of water by distillation to R1b,
- 25 (3) 25 kg/h of BD to R1a, containing 0.25% C2BU, which has been treated by contact with alumina in order to remove water and TBP stabilizer,
- (4) 2 kg/h of recycled BD from column K2a in step (2) to R1a (stream 9), so that the entire BD feed to reactor R1 obtained is a stream of 27 kg/h containing 98% BD and a total of 2% C2BU and 1-butene,
- 30 (5) 14 kg/h of nickel(0) catalyst solution to R1a, obtained as described below in this example as stream 10a from column K2b.

The stream 8 drawn off from reactor R1b (54 kg/h) contains a total of 4% BD and C2BU, corresponding to a conversion of 94% BD, and also a total of 74% pentenenitriles, of which 33% is T3PN, 37% 2M3BN and small amounts of Z2M2BN and E2M2BN, in addition to other pentenenitrile isomers, and also the catalyst constituents and catalyst degradation products and MGN.

In a step (2), stream 8 is fed to a distillation column K2a which is operated as a rectifying column and is equipped with a falling-film evaporator, and also column internals having structured packing which generate 4 theoretical plates. Column K2a is operated at the top with a direct condenser which consists of a column section charged with random packing and having total collecting cup, pumped circulation system and external heat exchanger. Column K2a is operated at an absolute top pressure of 0.8 bar, top temperature 263 K and bottom draw temperature 393 K.

Via the top of column K2a is obtained stream 9 which is metered into the reactor R1a as a recycle stream as described at the outset. The reflux ratio at the top of column K2a is adjusted in such a way that stream 9 contains 0.1% 2M3BN.

Via the bottom of column K2a are obtained 52 kg/h of a stream 1b which contains 0.3% BD, 0.1% C2BU, 76% pentenenitriles and also additionally the catalyst constituents.

Within step (2), stream 1b is conducted into a distillation column K2b which is operated in stripping mode and is equipped with a falling-film evaporator, top condenser with postcondenser, and also column internals having structured packing which generate 4 theoretical plates. The column is operated at an absolute top pressure of 70 mbar, top temperature 333 K and bottom draw temperature 373 K.

At the gaseous top draw of column K2b, stream 11 is obtained (40 kg/h), containing 0.4% BD, 54% 2M3BN and 42% T3PN, and also, to a lesser extent, E2M2BN and Z2M2BN in addition to other pentenenitrile isomers.

Into column K2b are conducted 3 kg/h of a catalyst stream, containing a total of 45% pentenenitriles, 1.5% Ni(0) and the chelate ligand, obtained, for example, by reacting nickel(0)(cyclooctadienyl)<sub>2</sub> complex with the chelate phosphite 2.

Via the bottom of column K2b is obtained the catalyst stream 10, containing 1.2% Ni(0), 0.3% 2M3BN and 17% residual pentenenitriles. Stream 10 is partly recycled into reactor R1 (14 kg/h) (stream 10a). Another portion (stream 10b) (3.8 kg/h) is fed to a regeneration according to DE-A-103 51 002, in order to be used in the hydrocyanation of 3-pentenenitrile according to DE-A-102 004 004 683, or, if appropriate, recycled into the hydrocyanation of BD according to the process according to the invention.

In a step (3), stream 11 is conducted to a distillation column K3 which is equipped with circulation evaporator and top condenser, and also with structured packing which generate 45 theoretical plates. Column K3 is operated at an absolute top pressure of 1.0 bar, top temperature 395 K and bottom draw temperature 416 K.

5

In step (5), 24 kg/h of recycle stream 5 from column K5 are conducted into column K3, containing 70% T3PN, 14% 2M3BN and 7% Z2M2BN, and also small amounts of further pentenenitrile isomers.

10 Via the top of column K3 are obtained 30 kg/h of a stream 13 containing 1% T3PN, 85% 2M3BN, 8% Z2M2BN, and also a total of 3% BD and C2BU in addition to other pentenenitrile isomers and VCH. The reflux ratio of column K3 is adjusted in such a way that 1% T3PN is obtained overhead.

15 Via the bottom of column K3 are obtained 38 kg/h of stream 12 containing a total of 97% T3PN, C3PN and 4PN, and also approx. 10 ppm of 2M3BN and approx. 2% E2M2BN, and small amounts of MGN and also other pentenenitrile isomers.

In Example 2, the catalyst used for the isomerization is the chelate phosphite-based nickel(0) complex, as described for the hydrocyanation of BD in this example.

25 In a step (4), stream 13 is conducted, together with a catalyst recycle stream 3a and a catalyst supplementation stream, into a reactor R2, designed as a compartmented reactor having tubular characteristics and equipped with a preheater, by which the reaction mixture is heated to 383 K. As the sum of recycled catalyst and fresh catalyst, 12 kg/h of a mixture having 20% T3PN, 3% 2M3BN and other pentenenitrile isomers, 71% ligand mixture and 0.6% nickel(0), and also a small content of catalyst degradation products, are conducted into reactor R2.

30 As the product from reactor R2, 43 kg/h of stream 1 are obtained, containing 53% T3PN, 12% 2M3BN, corresponding to a conversion of 80% 2M3BN.

35 In a step (5), stream 1 is conducted into a distillation column K5 which is equipped with a falling-film evaporator, top condenser, reflux divider, gaseous side draw in the bottom region of the column, and also column internals which generate 30 theoretical plates. The column is operated at an absolute top pressure of 377 mbar, top temperature 355 K and bottom draw temperature 368 K.

40 In column K5, the recovered catalyst stream 3 (11 kg/h) is obtained via the bottom, containing 20% T3PN in addition to other pentenenitriles, approx. 1% MGN, and also 0.6% Ni(0) and 54% ligand. A small portion (stream 3b) is discharged to restrict the accumulation of catalyst deactivation components and MGN. To replace the amount of

catalyst discharged, sufficient fresh catalyst containing 40% pentenenitrile isomers, 1.2% Ni(0) and 55% ligand mixture is metered in so that the Ni(0) content in the catalyst feed to reactor R2 is kept at 0.6%.

- 5 In column K5, a stream 4 is obtained overhead (1.4 kg/h), containing a total of 18% BD and C2BU, 45% 2M3BN, 28% Z2M2BN, and also small amounts of vinylcyclohexene (VCH). The reflux ratio of column K5 is adjusted in such a way that 10 ppm of T3PN are present in stream 4. The draw rate of stream 4 from the top of column K8 is adjusted in such a way that 10% Z2M2BN and VCH are present in the top draw stream  
10 13 of distillation column K3.

- In column K5, a stream 5 is obtained via the gaseous side draw (24 kg/h) which, in addition to 3-pentenenitriles, comprises substantially the 2M3BN unconverted in the isomerization and, after condensation, is recycled in liquid form into column K3 as  
15 described above.

### Example 3:

- Example 3 is illustrated with reference to Figure 5.  
20

- In Example 3, a catalyst system based on nickel(0) complexes with a mixture of ligands is used for the hydrocyanation of butadiene. The ligand mixture for the hydrocyanation contains approx. 60 mol% of tri(m/p-tolyl) phosphite and 40 mol% of the chelate phosphite 2.  
25

- In a step (1), the following streams are conducted into a system composed of two reactors, R1a and R1b, each of capacity 12 l, each of which is equipped with a nozzle, impulse exchange tube, external pumped circulation system and in a heat exchanger disposed in the pumped circulation system to remove the energy of reaction, and are  
30 heated to 363 K:

- (1) 6 kg/h of liquid, unstabilized hydrogen cyanide freed of water by distillation to R1a,  
35 (2) 6 kg/h of liquid, unstabilized hydrogen cyanide freed of water by distillation to R1b,  
(3) 25 kg/h of commercial BD to R1a, containing 0.25% C2BU, which has been treated by contact with alumina in order to remove water and TBP stabilizer,  
40

(4) 2 kg/h of recycled BD from column K2a in step (2) to R1a (stream 9), so that the entire BD feed to reactor R1 obtained is a stream of 27 kg/h containing 98% BD and a total of 2% C2BU and 1-butene,

- 5       (5) 14 kg/h of nickel(0) catalyst solution to R1a, obtained as described below in this example as stream 10a from column K2b.

The stream 8 drawn off from reactor R1b (54 kg/h) contains a total of 4% BD and C2BU, corresponding to a conversion of 94% BD, and also a total of 74%  
10    pentenenitriles, of which 33% is T3PN, 37% 2M3BN and small amounts of Z2M2BN and E2M2BN, other pentenenitrile isomers, and also the catalyst constituents and catalyst degradation products and MGN.

In a step (2), stream 8 is fed to a distillation column K2a which is operated as a  
15    rectifying column and is equipped with a falling-film evaporator, and also comprises column internals having structured packing which generate 4 theoretical plates. Column K2a is operated at the top with a direct condenser which consists of a column section charged with random packing and having total collecting cup, pumped circulation system and external heat exchanger. Column K2a is operated at an  
20    absolute top pressure of 0.8 bar, top temperature 263 K and bottom draw temperature 393 K.

Via the top of column K2a is obtained stream 9 which is metered into the reactor R1a as a recycle stream as described at the outset. The reflux ratio at the top of column  
25    K2a is adjusted in such a way that stream 9 contains 0.1% 2M3BN.

Via the bottom of column K2a are obtained 52 kg/h of a stream 1b which contains 0.3% BD, 0.1% C2BU, 76% pentenenitriles and also additionally the catalyst constituents.

30    Within step (2), stream 1b is conducted into a distillation column K2b which is operated in stripping mode and is equipped with a falling-film evaporator, top condenser with postcondenser, and also column internals having structured packing which generate 4 theoretical plates. The column is operated at an absolute top pressure of 70 mbar, top temperature 333 K and bottom draw temperature 373 K.

35    At the gaseous top draw of column K2b, stream 11 is obtained (40 kg/h), containing 0.4% BD, 54% 2M3BN and 42% T3PN, and also, to a lesser extent, E2M2BN and Z2M2BN in addition to other pentenenitrile isomers.

40    Into column K2b are conducted 5 kg/h of a catalyst stream which is obtained as described in Example 1 of DE-A-102004004683 as the bottom draw of column K4 from

step (4) of Example 2, containing a total of 45% pentenenitriles, 1.1% Ni(O), 38% ligand mixture and approx. 12% ADN.

5 Via the bottom of column K2b is obtained catalyst stream 10 containing 1.2% Ni(O), 0.3% 2M3BN and 17% residual pentenenitriles. Stream 10 is recycled partly into reactor R1 (14 kg/h) (stream 10a). Another portion (stream 10b) (3.8 kg/h) is fed to a regeneration according to DE-A-103 51 002, in order to be used in the hydrocyanation of 3-pentenenitrile according to DE-A-102 004 004 683.

10 In a step (3), stream 11 is conducted to a distillation column K3 which is equipped with circulation evaporator and top condenser, and also with structured packing which generate 45 theoretical plates. Column K3 is operated at an absolute top pressure of 1.0 bar, top temperature 395 K and bottom draw temperature 416 K.

15 In step (6), 28 kg/h of recycle stream 5 from column K6 are conducted into column K3, containing 72% T3PN, 15% 2M3BN and 8% Z2M2BN, and also small amounts of further pentenenitrile isomers.

20 Via the top of column K3 are obtained 30 kg/h of a stream 13 containing 1% T3PN, 85% 2M3BN, 8% Z2M2BN, and also a total of 3% BD and C2BU, and further pentenenitrile isomers. The reflux ratio of column K3 is adjusted in such a way that 1% 3PN is obtained overhead.

25 Via the bottom of column K3 are obtained 38 kg/h of stream 12 containing a total of 97% T3PN, C3PN and 4PN, and also approx. 10 ppm of 2M3BN and approx. 2% E2M2BN, and small amounts of MGN and further pentenenitrile isomers.

30 In Example 3, a catalyst system based on nickel(0) complexes with a mixture of ligands is used for the isomerization of 2M3BN to T3PN. The ligand mixture for isomerization (referred to hereinbelow as isomerization ligand) comprises mixed phosphite ligands of the P(OR)(OR')(OR'') class having randomly distributed R, R', R'' from the group of phenyl, m-tolyl, p-tolyl, o-tolyl, at least 80 mol% of the sum of the R, R', R'' radicals being m-tolyl and p-tolyl radicals. Such ligand mixtures are obtained in the reaction of a mixture of m- and p-cresol (having a mixing ratio of 2:1) of m- relative to p-cresol with a phosphorus trihalide. The promoter used for the isomerization reaction is zinc chloride,  
35 as described in US 3,676,481, US 3,852,329 and US 4,298,546.

40 In a step (4), stream 13 is conducted, together with a catalyst recycle stream 3a and a catalyst supplementation stream, into a reactor R2, designed as a compartmented reactor having tubular characteristics and equipped with a preheater, by which the reaction mixture is heated to 383 K. As the sum of recycled catalyst and fresh catalyst, 12 kg/h of a mixture having 20% T3PN, 3% 2M3BN and other pentenenitrile isomers,

71% isomerization ligand and 0.6% nickel(0), and also a small content of catalyst degradation products, are conducted into reactor R2.

5 The product obtained from reactor R2 is 43 kg/h of stream 1 containing 53% T3PN, 12% 2M3BN, corresponding to a conversion of 80% 2M3BN.

10 In a step (5), stream 1 is conducted into an evaporator stage B5 which is equipped with forced-circulation evaporator and top condenser. The evaporator stage B5 is operated at an absolute pressure of 510 mbar, bottom draw temperature 403 K and condensation temperature 366 K.

15 In evaporator stage B5, the recovered catalyst stream 3 (11 kg/h) is obtained via the bottom, containing 20% T3PN in addition to other pentenenitriles, approx. 10% MGN, and also 0.5% Ni(0) and 61% ligand mixture. A small portion (stream 3b) is discharged to restrict the accumulation of catalyst deactivation components and MGN. To replace the amount of catalyst discharged, sufficient fresh catalyst, containing approx. 15% pentenenitrile isomers, approx. 2.0% Ni(0), approx. 70% isomerization ligand and the zinc chloride promoter in a concentration which corresponds to a molar ratio of  $\text{ZnCl}_2$  to nickel(0) of approx. 5, is metered in so that the Ni(0) content in the catalyst feed to reactor R2 is kept at 0.6%.

25 In the evaporator stage B5, stream 2 is obtained at the top condenser (25 kg/h), containing 1% BD, 68% T3PN, 16% 2M3BN and further pentenenitriles, and also small amounts of VCH.

30 In a step (6), stream 2 is conducted into distillation column K6 which is operated as a rectifying column and is equipped with a circulation evaporator, top condenser, and also column internals which generate 30 theoretical plates. The column is operated at an absolute top pressure of 340 mbar, top temperature 357 K, 313 K in the condenser and bottom draw temperature 373 K.

At the condenser of column K6, the gas phase obtained is approx. 100 l (STP)/h of a stream which consists substantially of BD.

35 In column K6, the liquid phase obtained at the top condenser is a stream 4 (1.1 kg/h), containing a total of 5% BD and C2BU, 50% 2M3BN, 30% Z2M2BN, and also small amounts of vinylcyclohexene (VCH). The reflux ratio of column K6 is adjusted in such a way that 1 ppm of T3PN is present in stream 4. The draw rate of stream 4 from the top of column K6 is adjusted in such a way that a total of 10% Z2M2BN and VCH are present in the feed to reactor R2.

In column K6, a stream 5 is obtained via the bottom (24 kg/h) which, in addition to 3-pentenitriles, comprises substantially the 2M3BN unconverted in the isomerization, and is recycled into column K3 as described above.

#### 5 Example 4:

Example 4 is illustrated with reference to Figure 6.

10 In Example 3, a catalyst system based on nickel(0) complexes with a mixture of ligands is used for the hydrocyanation of butadiene. The ligand mixture for the hydrocyanation contains approx. 80 mol% of tri(m/p-tolyl) phosphite and 20 mol% of the chelate phosphite 2 (see Example 2).

15 In a step (1), the following streams are conducted into a system composed of three continuous stirred tanks R1a, R1b and R1c connected in series, each of capacity 10 l, which are heated to 373 K:

- 20 (1) 5.2 kg/h of liquid, unstabilized hydrogen cyanide freed of water by distillation to R1a,
- (2) 4.0 kg/h of liquid, unstabilized hydrogen cyanide freed of water by distillation to R1b,
- 25 (3) 20 kg/h of 1 BD as stream 9 from the condenser of evaporator B1 in step (2), containing 92% BD, 2% T3PN, 4% 2M3BN and approx. 2% C2BU to R1a,
- (4) 4.1 kg/h of nickel(0) catalyst solution to R1a, obtained as described below in this example, as stream 3a from evaporator stage B5 in step (5),
- 30 (5) 3.7 kg/h of nickel(0) catalyst solution to R1a, obtained as described in Example 3 of the German patent application with the title "Preparation of dinitriles" to BASF AG (B03/0525) as the bottom draw of column K4 from step (4) of Example 2, containing a total of 45% pentenenitriles, 1.1% Ni(0), 38% ligand mixture and approx. 12% ADN.

35

Reactor R1c is operated as a postreactor with the effluent from reactor R1b at 353 K.

Stream 8 drawn off from reactor R1c (37 kg/h) contains 1% BD, corresponding to a conversion of 98% BD, and also a total of 82% pentenenitriles, of which 36% is T3PN, 40 44% 2M3BN and small amounts of Z2M2BN and E2M2BN, and also the catalyst constituents and catalyst degradation products and MGN and further pentenenitrile isomers.

In a step (2), stream 8 is fed to an evaporator stage B1 which is equipped with a circulation evaporator. The evaporator stage B1 is operated at the top with a condenser which is flushed with condensed material from the reflux vessel. The evaporator stage  
5 B1 is operated at an absolute top pressure of 0.6 bar, condensation temperature 253 K and bottom draw temperature 363 K.

In the condensate collecting vessel of evaporator stage B1, 19.5 kg/h of commercial  
10 BD containing 0.25% C2BU are metered in, which has been treated by contact with molecular sieve, the water content of the BD used having been removed to less than 10 ppm by weight of water.

From the condensate collecting vessel of evaporator stage B1, stream 9 is drawn off as the sum of recycled and freshly metered butadiene, and recycled to reactor R1a as  
15 described above.

Via the bottom of evaporator stage B1 are obtained 37 kg/h of a stream 11b which contains 1% BD, 82% pentenenitriles and also additionally the catalyst constituents.

20 In a step (4), stream 11b is conducted into a reactor R2, heated to 383 K and designed as a stirred tank with downstream delay zone, and 2M3BN is isomerized to T3PN in the presence of the nickel catalyst.

A pentenenitrile recycle stream 5 is conducted into reactor R2 (10 kg/h) and is obtained  
25 in step (6) in column 6 as the bottom product containing 60% 2M3BN, a total of 10% T3PN with further pentenenitrile isomers, and also VCH and small amounts of BD.

From reactor R2, a stream 1 is obtained (45 kg/h) containing 62% T3PN and 14%  
30 2M3BN, corresponding to a conversion of 70% 2M3BN to T3PN, and also the catalyst components.

In a step (5), stream 1 is conducted into an evaporator stage B5 which is equipped with a falling-film evaporator and condenser and is operated at an absolute pressure of  
35 50 mbar and bottom draw temperature 393 K.

From the condenser of the evaporator stage B5, a stream 2 is obtained (38 kg/h), containing 91% pentenenitrile isomers and also approx. 1% BD and, to a lesser extent, E2M2BN, Z2M2BN and VCH.

40 Via the bottom of the evaporator stage B5, catalyst stream 3 is obtained (7.2 kg/h), containing 1.2% Ni(O), 0.1% 2M3BN and 15% residual pentenenitriles. Stream 3 is partly (stream 3a) recycled into reactor R1 (4.1 kg/h). The remainder (stream 3b) is fed

to a regeneration according to DE-A-103 51 002, and can be used after the regeneration, for example, in a hydrocyanation of 3-pentenitrile as in Example 2 of DE-A-102 004 004 683, or used again as the catalyst in the process according to the invention for hydrocyanating butadiene, if appropriate after removal of zinc chloride.

5

In a step (3), stream 2 is conducted to a distillation column K3 which is equipped with a forced-circulation evaporator and top condenser, and also with column internals which generate 30 theoretical plates. Column K3 is operated at an absolute top pressure of 120 mbar, top temperature 334 K and bottom draw temperature 352 K.

10

Via the top of column K3 are obtained 10 kg/h of a stream 13 containing 5% T3PN, 60% 2M3BN, 4% Z2M2BN, and also a total of 4% BD and C2BU, and a remainder of predominantly VCH. The reflux ratio of column K3 is adjusted in such a way that 5% T3PN are obtained overhead.

15

Via the bottom of column K3 are obtained 27 kg/h of stream 12 containing a total of 98% T3PN, C3PN and 4PN, and also approx. 1000 ppm of 2M3BN and approx. 2% E2M2BN.

20

In a step (6), stream 13 is conducted into a distillation column K6 which is operated as a rectifying column and is equipped with a forced-circulation evaporator, top condenser, reflux divider, and also column internals having structured packing which generate 15 theoretical plates. Column K6 is operated at an absolute top pressure of 380 mbar, top temperature 361 K and bottom draw temperature 365 K.

25

In column K6, a liquid stream 4 is obtained overhead (0.6 kg/h), containing a total of 4% BD and C2BU, 54% 2M3BN, 38% Z2M2BN, and also 2.5% vinylcyclohexene (VCH). The draw rate of stream 4 from the top of column K6 is adjusted in such a way that a total of 30% Z2M2BN and VCH are present in the top draw stream 13 of column

30

K3. In column K6, a gaseous stream is obtained at the top condenser operated as a partial condenser (195 l (STP)/h) which comprises substantially BD.

35

In column K6, stream 5 is obtained via the bottom (9.4 kg/h) which, in addition to 3-pentenitriles, comprises substantially the 2M3BN unconverted in the isomerization and is recycled into the isomerization reactor R2.

#### Example 5:

Example 5 is illustrated with reference to Figure 7.

40

In Example 5, a catalyst system based on nickel(0) complexes with a mixture of ligands is used for the hydrocyanation of BD. The ligand mixture for the hydrocyanation

contains approx. 80 mol% of tri(m/p-tolyl) phosphite and 20 mol% of the chelate phosphonite 1 (see Example 1).

5 In a step (1), the following streams are conducted into a system composed of two continuous stirred tanks R1a and R1b connected in series, each of capacity 50 l, which are heated to 363 K:

- 10 (1) 18 kg/h of liquid, unstabilized hydrogen cyanide freed of water by distillation in equal portions to reactors R1a and R1b,
- (2) 62 kg/h of BD as stream 9 from the top of evaporator B1 in step (2), containing 87% BD, 3% T3PN, 6% 2M3BN and approx. 2% C2BU to reactor R1a,
- 15 (3) 61 kg/h of nickel(0) catalyst solution, obtained as described below in this example, as stream 3a from evaporator stage B5 in step (5) to reactor R1a,
- (4) 6.7 kg/h of nickel(0) catalyst solution to R1a, obtained as described in Example 1 of the German patent application with the title "Preparation of dinitriles" to BASF AG (B03/0525) 1, is obtained as the bottom draw of column K4 from step (4) of Example 2, containing a total of 45% pentenenitriles, 1.1% Ni(0), 38% ligand mixture, and also approx. 12% ADN to reactor R1a, the butadiene stream and the catalyst stream being premixed before contacting with hydrogen cyanide.
- 20

25 The stream 8 drawn off from reactor R1b (177 kg/h) contains 11% BD, corresponding to a conversion of 66% BD, and also a total of 64% pentenenitriles, of which 32% is T3PN, 30% 2M3BN and small amounts of Z2M2BN and E2M2BN and further pentenenitrile isomers, and also the catalyst constituents and catalyst degradation products.

30 In a step (2), stream 8 is fed to an evaporator stage B1 which is equipped with a falling-film evaporator. The evaporator stage B1 is operated with a condenser at the top which is flushed with condensed material from the reflux vessel. The evaporator stage B1 is operated at an absolute top pressure of 1.3 bar, condensation temperature 278 K and  
35 bottom draw temperature 403 K.

Into the condensate collecting vessel of the evaporator stage B1 are metered 37 kg/h of commercial BD containing 0.25% C2BU which has been treated by contact with molecular sieve, the water content of the BD used having been removed to less than  
40 5 ppm by weight of water and the TBP stabilizer present in the BD used reaching the condensate collecting vessel and condenser flushing circuit in concentrations on the ppm scale.

From the condensate collecting vessel of the evaporator stage B1, stream 9 is drawn off as the sum of recycled and freshly metered BD and recycled to reactor R1a as described above.

5

Via the bottom of evaporator stage B1 are obtained 152 kg/h of a stream 11b which contains 0.9% BD, 16% 2M3BN, 51% T3PN and further pentenenitrile isomers, and also additionally the catalyst constituents. The composition of the bottom effluent of the evaporator stage allows a degree of conversion of 50% 2M3BN to T3PN in the bottom of the evaporator B1 to be concluded.

10

In a step (5), stream 11b is conducted into an evaporator stage B5 which is equipped with falling-film evaporator and condenser and is operated at an absolute pressure of 260 mbar and bottom draw temperature 383 K.

15

From the evaporator stage B5, a stream 2 is obtained in gaseous form (83 kg/h), containing 93% pentenenitrile isomers, and also approx. 1% BD and, to a lesser extent, E2M2BN, Z2M2BN and VCH. Stream 2 is conducted into distillation column K3 in step (3).

20

Via the bottom of evaporator stage B5 is obtained the catalyst stream 3 (69 kg/h), containing 0.6% Ni(0), 2% 2M3BN and 42% residual pentenenitriles. Stream 4 is for the most part recycled into reactor R1 (61.4 kg/h) (stream 3a). The remainder (stream 3b) is fed to a regeneration according to DE-A-103 51 002, and may be used, for example, in the hydrocyanation of 3-pentenenitrile, as described in Example 1 of DE-A-102 004 004 683.

25

In a step (3), stream 2 is conducted in gaseous form to a distillation column K3 which is equipped with a forced-circulation flash evaporator and top condenser, and also with structured packing which generate 30 theoretical plates. Column K3 is operated at an absolute top pressure of 80 mbar, top temperature 375 K and bottom draw temperature 343 K.

30

Via the top of column K3 are obtained 36 kg/h of a stream 13 containing 15% T3PN, 64% 2M3BN, 3% Z2M2BN, and also a total of 4% BD and C2BU, the remainder comprising predominantly VCH. The reflux ratio of column K3 is adjusted in such a way that 15% T3PN is obtained overhead.

35

Via the bottom of column K3 are obtained 47 kg/h of stream 12 containing a total of 98% T3PN, C3PN and 4PN, and also 100 ppm of 2M3BN and approx. 1% E2M2BN.

40

In a step (6), stream 13 is conducted into a distillation column K6 which is operated as a rectifying column and is equipped with a forced-circulation evaporator, top condenser, reflux divider, and also column internals having structured packing which generate 45 theoretical plates. The column is operated at an absolute top pressure of 320 mbar, condensation temperature 288 K and bottom draw temperature 363 K.

In column K6, a liquid stream 4 is obtained via the top (6.8 kg/h) containing a total of 10% BD and C2BU, 80% 2M3BN, 8% Z2M2BN, and also 0.5% vinylcyclohexene (VCH). The draw rate of stream 4 from the top of column K6 is adjusted in such a way that a total of 15% Z2M2BN and VCH is present in the top draw stream 3 of the column K3. In column K6, a gaseous stream is obtained at the top condenser operated as a partial condenser (263 l (STP)/h) which comprises substantially BD.

In column K6, stream 5 is obtained via the bottom (28.7 kg/h) which, in addition to 3-pentenitriles, comprises substantially the 2M3BN unconverted in the isomerization and is recycled into the hydrocyanation reactor R1.

#### Example 6:

Example 6 is illustrated with reference to Figure 8.

In Example 8, a catalyst system based on nickel(0) complexes with chelate phosphonite 1 as the ligand is used for the hydrocyanation of BD (see Example 1).

In a step (1), the following streams are conducted into a continuously operated stirred tank R1 of volume 30 l which is heated to 363 K:

- (1) 16 kg/h of liquid, unstabilized hydrogen cyanide freed of water by distillation,
- (2) 55 kg/h of BD as stream 9 from the top of evaporator B1 in step (2), containing 87% BD, 3% T3PN, 6% 2M3BN and approx. 2% C2BU,
- (3) 10 kg/h of nickel(0) catalyst solution, obtained as described below in this example, as stream 3a from evaporator stage B5 in step (5), containing a total of 42% pentenenitriles, 23% ligand, 0.9% nickel(0), and also in each case approx. 10% ADN and MGN,
- (4) 4 kg/h of nickel(0) catalyst solution to R1, containing a total of 45% pentenenitriles, 1.5% Ni(0) and 48% ligand.

The stream 8 drawn off from reactor R1 (89 kg/h) contains 17% BD, corresponding to a conversion of 71% BD, and also a total of 73% pentenenitriles, of which 32% is T3PN,

36% 2M3BN and small amounts of Z2M2BN and E2M2BN, and also the catalyst constituents and the catalyst degradation products.

- 5 In a step (2), stream 8 is fed to an evaporator stage B1 which is equipped with a falling-film evaporator. The evaporator stage B1 is operated with a condenser at the top which is flushed with condensed material from the reflux vessel. The evaporator stage B1 is operated at an absolute top pressure of 1.3 bar, condensation temperature 278 K and bottom draw temperature 403 K.
- 10 Into the condensate collecting vessel of evaporator stage B1 are metered 34 kg/h of commercial BD containing 0.25% C2BU which has been treated by contact with alumina, the water content of BD used having been reduced to less than 10 ppm by weight of water and the TBP content to less than 10 ppm.
- 15 From the condensate collecting vessel of the evaporator stage, stream 9 is drawn off as the sum of recycled and freshly metered butadiene, and recycled to reactor R1a as described above.
- 20 Via the bottom of evaporator stage B1 are obtained 76 kg/h of a stream 5 which contains 0.8% BD, 12% 2M3BN, 69% T3PN and further pentenenitrile isomers, and also additionally the catalyst constituents. The composition of the bottom effluent of the evaporator stage corresponds to a degree of conversion of 75% 2M3BN to T3PN in the bottom of the evaporator stage B1.
- 25 In a step (5), stream 5 is conducted into an evaporator stage B5 which is equipped with a falling-film evaporator and condenser and is operated at an absolute pressure of 220 mbar and bottom draw temperature 381 K.
- 30 From the evaporator stage B5, a stream 2 is obtained in gaseous form (58 kg/h) containing 97% pentenenitrile isomers, and also approx. 1% BD and, to a lesser extent, E2M2BN, Z2M2BN and VCH.
- 35 Via the bottom of the evaporator stage B5 is obtained the catalyst stream 3 (17 kg/h) containing 0.9% Ni(0), 0.3% 2M3BN and 42% residual pentenenitriles. Stream 3 is for the most part recycled into reactor R1 (10 kg/h) (stream 3a). The remainder (stream 3b) is fed to a regeneration according to US 2003/0100442 and may, after the regeneration, be used in a hydrocyanation of 3-pentenenitrile or recycled into the process according to the invention, into the step for hydrocyanating BD.
- 40 Stream 2 is condensed and, in a step (3), conducted in liquid form to a distillation column K3 which is equipped with a forced-circulation evaporator and top condenser, and also with structured packing which generate 50 theoretical plates. Column K3 is

operated at an absolute top pressure of 200 mbar, top temperature 342 K and bottom draw temperature 366 K.

At the top of column K3, a stream 4 is obtained, containing 10% BD, 18% Z2M2BN, 68% 2M3BN, and also further pentenenitrile isomers and VCH. The reflux ratio of column K3 is adjusted in such a way that the top draw stream contains 18% Z2M2BN.

At a liquid side draw of column K3, 8 kg/h of a stream 13 are obtained, containing 0.5% T3PN, 85% 2M3BN, 5% Z2M2BN, 10% BD. Stream 13 is recycled into evaporator stage B1.

Via the bottom of column K3 are obtained 47 kg/h of stream 12 containing a total of 98% T3PN, C3PN and 4PN, and also 100 ppm of 2M3BN and approx. 1% E2M2BN.

All experiments below were carried out in a protective gas atmosphere.

Nickel(0)[o-isopropylphenyl<sub>0.8</sub> m-/p-tolyl<sub>3.2</sub> phosphite]<sub>18</sub>, (for short: isopropyl catalyst); corresponds to a solution of 1.0% by weight of nickel(0) with 19% by weight of 3PN and 80% by weight of o-isopropylphenyl<sub>0.8</sub> m-/p-tolyl<sub>3.2</sub> phosphite.

Examples of the continuous hydrocyanation of BD to 2M3BN/3PN

Example 7 (comparative): (BD/HCN ratio = 1.4:1)

2.11 mol of moist and stabilized butadiene (100 ppm of water, 100 ppm of TBP), 1.55 mol of HCN and 14 mmol of Ni in the form of the isopropyl catalyst are fed per hour into a pressure reactor (pressure: 15 bar, internal temperature 105°C, residence time: approx. 40 min/reactor). According to volumetric analysis, the HCN conversion is quantitative (Vollhard titration). The 2M3BN/3PN ratio of the reaction effluent is determined by GC chromatography (GC area percent). The 2M3BN/3PN ratio was 1.95/1. The loss of Ni(0) based on product of value formed was: 0.58 kg of Ni(0)/t of product of value (3PN/2M3BN).

Example 8: (BD/HCN ratio = 1.4:1)

2.13 mol of butadiene dried over a bed of 4 Å molecular sieve, 1.53 mol of HCN and 14 mmol of Ni in the form of the isopropyl catalyst are fed per hour into a pressure reactor (pressure: 15 bar, internal temperature 105°C, residence time: approx. 40 min/reactor). According to volumetric analysis, the HCN conversion is quantitative (Vollhard titration). The 2M3BN/3PN ratio of the reaction effluent is determined by GC chromatography (GC area percent). The 2M3BN/3PN ratio was 1.95/1. The loss of

Ni(0) based on product of value formed was: 0.14 kg of Ni(0)/t of product of value (3PN/2M3BN).

Example 9: (BD/HCN ratio = 1.2:1)

5

2.09 mol of butadiene dried over a bed of alumina, 1.67 mol of HCN and 14 mmol of Ni in the form of the isopropyl catalyst are fed per hour into a pressure reactor (pressure: 15 bar, internal temperature 105°C, residence time: approx. 45 min/reactor). According to volumetric analysis, the HCN conversion is quantitative (Vollhard titration). The 2M3BN/3PN ratio of the reaction effluent is determined by GC chromatography (GC area percent). The 2M3BN/3PN ratio was 1.95/1. The loss of Ni(0) based on product of value formed was: <0.10 kg of Ni(0)/t of product of value (3PN/2M3BN).

10

Examples of the continuous isomerization of 2M3BN to 3PN

15

Example 10:

A hydrocyanation effluent prepared in Example 8 is collected and freed distillatively of excess BD. The thus obtained mixture is heated to 130°C for one hour. After 0 and 30 min and after 1 h, GC samples are taken from the reaction mixture and analyzed by GC chromatography (GC area percent).

20

Time	2M3BN	E,Z-2M2BN	c,t-2PN	4PN	c,t-3PN	3PN/2M3BN
0 h	15.62	0.20	0.50	0.50	38.33	2.45
30 min	10.21	0.21	0.51	0.49	42.36	4.15
1 h	5.69	0.27	0.54	0.51	47.12	8.28

Examples of the incorrect isomerization of 2M3BN to 2M2BN by recycled hydrocyanation catalyst

25

Example 11:

From a catalyst reservoir, filled with 649 g of fresh isopropyl catalyst at t = 0 h, 100 g of isopropyl catalyst are withdrawn continuously and fed into a pressure reactor together with 2.14 mol of butadiene dried over a bed of alumina, and also 1.67 mol of HCN, per hour (pressure: 15 bar, internal temperature 105°C, residence time: approx. 45 min/reactor). According to volumetric analysis, the HCN conversion is quantitative (Vollhard titration). The product of value is removed continuously from the catalyst by means of a Sarnbay distillation and the thus obtained return catalyst is recycled into the reservoir. The reaction is operated for 50 h and the still hydrocyanation-active catalyst is discharged owing to beginning formation of the 2M2BN secondary component. The thus obtained catalyst is subjected to isomerization experiments:

30

35

## Example 12 (comparative):

- 10 g of isomerization catalyst are supplemented with 2M3BN (15 g) and heated at  
5 120°C for 5 h. At a conversion of 89% 2M3BN (GC area percent), 8.6% incorrect  
isomers (2M2BN) are found.

## Example 13:

- 10 n-Heptane (100 g) and adiponitrile (50 g) are added to the isomerization catalyst from  
Example 11 (100 g) and the mixture is stirred (15 min). After a phase separation  
(30 min), the lower phase is discharged. A portion of the upper phase (50 g,  
heptane+isomerization catalyst) is concentrated on a rotary evaporator. The residue  
(14 g, isomerization catalyst) is supplemented with 2M3BN (21 g) and heated at 120°C  
15 for 5 h. At a conversion of 95% 2M3BN (GC area percent), 2.0% incorrect isomers  
(2M2BN) are found.

## Example 14:

- 20 The residues of the upper phase from the first extraction (Example 12) are again  
admixed with adiponitrile (37.5 g) and stirred. After the phase separation, a portion of  
the upper phase is again concentrated on a rotary evaporator and the residue (9.3 g) is  
supplemented with 2M3BN (14 g). After 5 h at 120°C, a 2M3BN conversion of 94%  
(GC area percent) and an incorrect isomerization of 0.7% are found.

25

Examples of the incorrect isomerization of 2M3BN to 2M2BN by continuously used  
isomerization catalyst

## Example 15:

30

- A 2 l reactor is charged with 300 g of isopropyl catalyst which are admixed continuously  
with 450 g/h of 2M3BN and heated to 130°C. At a residence time of 60 min, reactor  
contents are withdrawn and worked up by distillation continuously, and the  
isomerization catalyst remaining in the bottom is recycled. The reaction is operated for  
35 50 h and the still isomerization-active catalyst is discharged owing to beginning  
incorrect isomerization of 2M3BN. The thus obtained catalyst is subjected to  
isomerization experiments:

## Example 16:

10 g of isomerization catalyst are supplemented with 2M3BN (15 g) and heated at 120°C for 5 h. At a conversion of 90% 2M3BN (GC area percent), 9.8% incorrect isomers (2M2BN) are found.

## Example 17:

n-Heptane (100 g) and adiponitrile (50 g) are added to the isomerization catalyst from Example 16 (100 g) and the mixture is stirred (15 min). After a phase separation (30 min), the lower phase is discharged. A portion of the upper phase (50 g, heptane+isomerization catalyst) is concentrated on a rotary evaporator. The residue (14 g, isomerization catalyst) is supplemented with 2M3BN (21 g) and heated at 120°C for 5 h. At a conversion of 93% 2M3BN (GC area percent), 2.4% incorrect isomers (2M2BN) are found.

## Example 18:

The residues of the upper phase from the first extraction (Example 17) are again admixed with adiponitrile (37.5 g) and stirred. After the phase separation, a portion of the upper phase is again concentrated on a rotary evaporator and the residue (9.3 g) is supplemented with 2M3BN (14 g). After 5 h at 120°C, a 2M3BN conversion of 93% (GC area percent) and an incorrect isomerization of 0.6% are found.